PHOSPHORUS BIOGEOCHEMISTRY IN MELTWATER PONDS OF VICTORIA LAND, ANTARCTICA

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Abstract

Phosphorus plays an essential role in the biochemistry of all living organisms, and understanding factors controlling its availability in an ecosystem can provide insight into how the ecosystem will respond to change. Freshwater ecosystems in Antarctica are important biodiversity elements, containing vibrant microbial communities dominated by benthic cyanobacterial mats. Productivity in meltwater ponds can become limited by nutrient availability, and inland aquatic systems are typically P deficient.

In order to understand phosphorus (P) biogeochemistry in meltwater ponds in Victoria Land, the distribution and speciation of P was determined in ponds at 7 locations, and processes which influence P concentration in the water column were investigated. The biogeochemical cycle concept has been applied to the results as a tool to interpret P behaviour. This involved identification of the key reservoirs that hold P within the pond ecosystem, and the processes which can transfer P between these reservoirs.

Sediment, soil, water and benthic microbial mats were identified as important reservoirs in the ponds. Microbial mats can accumulate P to concentrations over 2 g/kg, and often had higher concentrations of P than soils and sediments. Soils consistently had higher P concentrations than sediments, and comparatively little P was present in pond waters. Concentration and pond structure data were used to create a conceptual model of P distribution in meltwater ponds, which revealed sediments are the major reservoir of P in these systems. Saturated soils are the next largest reservoir of P, followed by microbial mats then the pond water.

Sediments are the major source of P to meltwater ponds. This is demonstrated by low total P concentrations in sediments relative to adjacent soils. Transects from pond shorelines reveal that both reactive and apatite P fractions in sediments are transported into ponds, and that soils within 2 m from pond edges can also act as a P source. It is not clear whether P from marginal soils is provided to the pond during inundation. Wind-blown dust contains high concentrations of labile P relative to soils, and is an intermittent source of P to ponds. Significant quantities of P are lost from pond ecosystems via wind transport of foam and desiccated mats.

There is significant biotic control over DRP concentrations in pond water columns. Benthic microbial mats are the main consumers of DRP in most ponds, and are capable of sequestering DRP from the water column in lit conditions. In the dark, mats act as a source of DRP to pond water. Circadian cycles drive changes in physico-chemical conditions present in ponds, but have little effect of DRP concentrations. Biological activity seems to drive short term fluctuations in DRP concentrations occur throughout the day.

A systematic pattern is apparent between pond location and P abundance. High P concentrations exist in all of the reservoirs of low elevation coastal ponds, while inland pond systems at high elevation generally contained very low P concentrations. Soil P concentrations correlate inversely with pond elevation, as do inorganic N:P ratios. Soil P composition is constrained by the composition of its parent material, and is thus a product of bedrock geology and landscape history. Sediment P composition derives from an initial composition similar to the soil, which is altered by weathering and accumulation of biological and inorganic debris. Therefore the bedrock geology and landscape history of an area are major determinants of P abundance in ponds.

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Abbreviations

ATP	Adenosine triphosphate
BI	Bratina Island
CE	Cape Evans
CR	Cape Royds
DIC	Dissolved inorganic carbon
DNA	Deoxyribose nucleic acid
DO	Dissolved oxygen
DOP	Dissolved organic phosphorus
DRP	Dissolved reactive phosphorus
EDS	Energy-dispersive X-ray spectroscopy
ESEM	Environmental scanning electron microscopy
HPIC	High pressure ion chromatography
HPP	Hut Point Peninsula
LWV	Lower Wright Valley
MIS	McMurdo Ice Shelf
MO-P	Metal oxide adsorbed and organic phosphorus
MV	Miers Valley
PP	Particulate phosphorus
RO-P	Reducible oxide adsorbed phosphorus
TDP	Total dissolved phosphorus
TIN	Total inorganic nitrogen
UWV	Upper Wright Valley
XRD	X-ray diffraction

Chapter 1:
Introduction

Fig. 1.1 An ice covered meltwater pond in the Labyrinth, Upper Wright Valley, in January 2012. Image courtesy of Ian Hawes.

1.1 Thesis objective

This thesis aims to evaluate the major components of the phosphorus (P) cycle in meltwater ponds in the Ross Sea region of Antarctica. Phosphorus availability is essential for primary production in aquatic systems. Understanding the P cycle, and the factors regulating P availability provides an important background, useful in managing aquatic systems, and assessing their susceptibility to change.

1.2 Research background

1.2.1 Antarctic meltwater systems

The continent of Antarctica contains some of the most extreme environments on Earth (Campbell & Claridge 1987). Ice sheets cover the majority of the continent, with only 0.3 % of the land mass exposed rock (Fox & Cooper 1994). The climate is renowned for its exceptionally cold temperatures, high winds and severe aridity, as well as extremes in solar radiation and temperature. None-the-less, a remarkable array of life forms inhabit the continent.

The presence of water is essential for life, and aquatic systems that form from meltwater create habitats which (seasonally or year-round) have abundant moisture. These aquatic systems can be divided into three main groups: rock-based systems; including rock based ponds, streams, rivers, and the iconic large lakes, ice-based systems; supraglacial streams, ponds and cryoconites, and subglacial lakes and rivers (Priscu & Foreman 2009). There have been reports of life found in all of these types of meltwater systems (Broady 1989, Lanoil *et al.* 2009, Stanish *et al.* 2013).

Victoria Land is the region of Antarctica bound to the east by the Ross Sea and Ross Ice shelf, and to the west by Wilkes Land. Victoria Land stretches from Cape Adare in the north to Minna Bluff in the South, and thus covers a wide range of elevations and distances from the coast, from sea level to the polar plateau, as well as a range of latitudes. In addition, a variety of geologies and rock types occur throughout the region, including the McMurdo Volcanics, Beacon Supergroup sandstones, Ross Supergroup schists and marbles, granite, Ferrar dolerite, Jurassic basalts and coal measures (Campbell & Claridge 1987). Meltwater systems of all types occur throughout this region, and include the McMurdo Dry Valley Lakes, Antarctica's longest river

the Onyx River, streams, cryoconites, and many hundreds of rock based meltwater ponds (Vincent & Laybourn-Parry 2008).

Rock based ponds, referred to henceforth as meltwater ponds, are common in ice-free landscapes, forming from collection of snow and glacial melt in topographical depressions (Fig. 1.1). These ponds often have closed drainage basins (Torii *et al.* 1988), and the water mass balance is dependent on inflow from ice melt, and ablation and evaporation from the pond surface. Pond dimensions range from 1 m to more than 100 m (Demora *et al.* 1994). Some ponds that still exist today, were first documented by parties of the first polar expeditions (Broady 1989, Murray 2011). Elsewhere, documented changes in pond level highlight the vulnerability of these systems to changes in snow accumulation and melt regimes (Hawes *et al.* 2014). Meltwater systems tend to be oligotrophic (Lyons & Finlay 2008), experience long periods of snow and ice cover in winter, and can have low annual inputs of photosynthetically active radiation (Bell & Laybourn-Parry 1999). Solutes delivered to closed basin ponds have limited pathways to leave. Pond chemistry is driven by catchment geology, aerosol derived soluble salts in the catchment (Takamatsu *et al.* 1998), the biological processes that occur within the pond (Hawes *et al.* 2014), and the physical changes that ponds undergo each season (Wait, 2009). Ponds from different areas can exhibit varying nutrient and major ion compositions (Torii *et al.* 1988); however, neighbouring systems from the same area can also have order of magnitude differences in conductivity, and unit differences in pH, as well as different major ion and nutrient compositions (Healy *et al.* 2006, Wait *et al.* 2006, Priscu & Foreman 2009). These ponds have been of scientific interest for many years, due to their wide distribution, diverse characteristics and compositions, and the thriving microbial ecosystems they hold.

Meltwater ponds are important biodiversity elements in Antarctica, hosting some of the highest concentrations of biomass found in terrestrial ecosystems on the continent (Howard-Williams *et al.* 1989). They provide a benthic and a planktonic habitat, and the microbial mats that colonise the benthos tend to dominate biomass. Cyanobacteria are the major component of the mats, and the principal primary producers in meltwater pond ecosystems (Hawes *et al.* 1993). The presence and size of a pond is dependent on seasonal input of meltwater, hence these habitats are susceptible to changes in melt patterns. There is evidence of changes in melt regimes in the McMurdo Dry Valleys, with documented increases in the level of many of the large lakes

(Bomblies *et al.* 2001). It is difficult to predict what changes may take place to meltwater ponds with changes in climate. However, if an increase in temperature results in greater availability of meltwater, the occurrence and size of meltwater ponds may also increase. If habitat sizes increase, there may be little change to overall productivity if nutrient concentrations are too low to promote growth.

1.2.2 Nutrients and meltwater ecology

For life to inhabit an environment, the requirements of organisms' energetic, hydration and nutritional needs must be met. Nutrients are elements essential to the biochemical reactions that allow an organism to survive. The term macronutrients generally refers to carbon, nitrogen and phosphorus, which are required at relatively high concentrations by organisms, while micronutrients such as iron are needed in much smaller amounts. A seminal paper by Alfred Redfield described an average ratio of C:N:P of 106:16:1 that was measured in marine phytoplankton from many locations. Several variations close to this ratio have been proposed, with a recent comparison of freshwater and marine sestons, showing a ratio of 166:20:1 at large spatial scales (Sterner *et al.* 2008). This compositional ratio differs slightly between species, but is often used as an approximation of the requirements of primary producers. Often, when nutrients are present in an environment at concentrations that deviate significantly from the Redfield ratio, it can suggest that one of the elements is difficult for organisms to acquire. When the availability of a nutrient restricts primary production in a system, the system is said to be limited by that nutrient. Many aquatic systems worldwide are either P or N limited, and this is seen in meltwater ponds (Priscu & Foreman 2009).

Nutrients take part in global biogeochemical cycles, in which they are transferred between reservoirs (Berner & Berner 1996). These reservoirs are all the components of an ecosystem which can contain the nutrient and typically, within each reservoir, the nutrient can exist in number of forms. A range of physical, chemical and biological processes can transport and transfer nutrients between reservoirs, and between different chemical forms. Often the elements undergo a series of processes that can include returning it to reservoirs and forms that it has previously occupied; hence "biogeochemical cycling" is also the term applied to ecosystems. Ecosystems are normally open systems, and so their nutrient cycles tend to include sources and sinks of the nutrient, as well as the reservoirs holding the nutrient, and the transfer processes

taking place. Knowledge of the nutrient cycles for an ecosystem allows identification of the drivers of the ecosystem, and an understanding of how it may react to change.

Nutrient concentrations in Antarctic meltwater systems vary from non-detectable, to many mg/L, and nutrient availability has been strongly suggested as a factor limiting primary productivity in these systems (Vincent, 2008). Meltwater ponds in close proximity can have variable biomass, primary production rates, and nutrient compositions, despite similar irradiance and temperature regimes (Vincent & Laybourn-Parry 2008, Priscu & Foreman 2009). Some of the richest systems with respect to nutrients are found near seabird colonies, which can have abundant N and P, and high rates of primary production (Vincent & Vincent 1982). Additionally, planktonic populations in some ponds have been shown to respond strongly to nutrient additions (Vincent & Vincent 1982, Hawes *et al.* 1993). Studies of nutrient concentrations in different locations reveal a trend of increasing N availability inland, due to nitrogen-rich upper atmosphere aerosol deposition with precipitation. Meanwhile P is typically present in coastal areas, but often undetectable inland (Vincent & Howard-Williams 1994). This pattern suggests a general rule of N being the most likely nutrient to limit growth in coastal systems, and P in inland systems. In P-limited systems, changes in P availability will directly affect primary production. The role of P as an essential nutrient, and a factor limiting growth in some ponds, makes knowledge of the P cycle important.

1.2.3 Phosphorus biogeochemistry

Phosphorus is a Group 15 element and is essential in the biochemistry of all living cells. It makes up the phosphate-sugar backbone of both deoxyribose and ribose nucleic acids, is a component of the phospholipids that form cell walls, and the phosphorus – oxygen bonds of adenosine triphosphate store and transport the chemical energy required for cellular metabolism. Compounds containing P that are synthesized by biological reactions are termed ‘biotic P’. This includes organic P molecules, such as DNA, phospholipids and ATP as mentioned above, which have a phosphate group incorporated into a carbon-containing molecule, and also condensed phosphates which include pyro- and polyphosphates, which are synthesized by organisms for P storage. These organic P molecules have varying reactivities, with condensed phosphates being readily hydrolysable, whilst phosphonates have a direct carbon to phosphorus bond and are

considered extremely stable (Turner, 2005). Primary production can become limited by the amount of P available, where other resource requirements are met.

The P cycle is comprised of P transfer between solid, biological and dissolved phases in an ecosystem. Throughout these transfers, phosphorus occurs almost exclusively in the valance state of P^{5+}. Phosphorus is predominantly found in the lithosphere as apatite ($Ca_4(PO_4)_3(OH,Cl,F)$). Apatite is a calcium phosphate mineral which is typically found in rocks and sediments, at concentrations of 0.1 to 1 vol % (Bengtsson & Sjoberg 2009). The hydroxide, chloride and fluoride anions are able to substitute for each other in the structure, and the apatite with fluoride ions 'flourapatite' is the most resistant to chemical degradation. The weathering of apatite is the principle source of P to ecosystems, and can occur after the apatite-bearing substrate is exposed. Once released from its primary mineral form, phosphate is very reactive, and can quickly form associations with other components which reduce its bioavailability. It can form complexes with cations in solution, precipitate with metals (for example, Ca, Mg, Fe, Al and Mn), it has a high adsorption affinity for (hydr)oxides of iron (Cornell & Schwertmann 2003), aluminium (Hesse 1973) and manganese (Kawashima *et al.* 1986), and is a component of organic matter. These different chemical forms of P have varying potential to be mobilized or made available to organisms, depending on environmental conditions. Dissolved phosphate ions are easily sequestered by organisms, while P in other forms generally requires a process to release it into solution as PO_4^{3-} to become available. P weakly sorbed to some surfaces via electrostatic interactions may be desorbed by ion exchange, while P strongly sorbed to metal oxides through chemical bonds may require dissolution of the sorbing phase (which occurs for some metal oxides in reducing conditions), or removal by competing ions (such as hydroxide in high pH conditions) to be released (Cornell & Schwertmann 2003). Therefore, processes such as leaching, adsorption, weathering, biological uptake and remineralisation can redistribute and transport P into various reservoirs and chemical phases.

Measurement of P concentration and speciation in environmental samples has been a subject of considerable research, including water, biomass, soil and sediment. P is often difficult to measure as a chemical species in solutions or solids, and is generally classified into operationally defined fractions. The standard method to measure solution P is spectrophotometrically as the PO_4^{3-} ion (APHA 4500-P Method E). The method causes a phosphate complex to form with

antimony and molybdate ions in acid medium, followed by reduction of the complex by ascorbic acid to a blue complex ion. The acidic conditions of the reaction are able to hydrolyse phosphate from other forms, such as condensed phosphates. Hence dissolved P is typically reported as dissolved reactive phosphorus (DRP) rather than PO_4^{3-} – P, and includes PO_4^{3-} and all other P that will react during the analysis. Many analytical techniques rely on transforming P forms in a sample into dissolved PO_4^{3-} ions, and then analyzing the solution by this same photometric method. For example, total dissolved P (TDP) is analysed by performing an acid persulfate digestion on a filtered water sample (APHA 4500-P Method B5), followed by the molybdenum blue colorimetric method. Dissolved organic P (DOP) can then be calculated, and is generally defined as the difference between TDP and DRP, and includes any organic or biotic compounds such as polyphosphates which have been converted to DRP in the digestion step.

In soils and sediments, P is present in more chemical forms, hence determination of P concentrations and fractionation is more complex. The biogeochemical significance of P in soil and sediments is dependent on its mineral or binding form and its reactivity. The environmental conditions that occur in the soil or sediment can affect solubility of P minerals and binding phases, thus are also important in determining potential bioavailability. A number of techniques have been developed to study associations of P in soil and sediment samples, of which sequential extractions are the most widely utilised. Sequential extractions are employed to target different chemical and mineral fractions that the element of interest may associate with in the sample. This is done by reacting a sample with increasingly aggressive reagents, and analyzing for the element after each step. Sequential extraction techniques have several limitations, including redistribution of targeted elements into other phases during dissolution steps, and also dissolution of non-target phases in some steps (Ruban *et al.* 1999). For P, commonly targeted fractions include an easily mobilized fraction that is either soluble or released by ion exchange, P associated with organic material, a fraction that is adsorbed to metal (hydr-)oxides, which can be further distinguished by the oxide reactivity, mineral P, and residual phases (Ruban *et al.* 1999). Knowledge of the concentration and speciation of P in an ecosystem can provide insight into its potential availability to organisms.

1.3 Research questions

The thesis objective will be met by addressing the following four questions.

1.3.1 What is the natural abundance of P in each component of a meltwater pond?

Numerous studies have focused on P abundance in the water reservoir of meltwater ponds. Measurements of DRP, DOP and particulate P (PP) range from non-detectable to hundreds of µg/L in some systems, and a general trend is observed of high N:P ratios in inland ponds, and low N:P ratios in coastal systems (Torii *et al.* 1988, Vincent & Howard-Williams 1994). Measurements of P abundance in water, soil and sediment reservoirs of soil and stream ecosystems have been reported, with dry valley soils and streams containing up to 1500 mg/kg and >1 mg/L total P respectively (Howard-Williams *et al.* 1997, Blecker *et al.* 2006, Bate *et al.* 2008, Welch *et al.* 2010).

To date, no study has characterized P abundance and distribution holistically, across all components of a meltwater pond environment. The pond water, microbial mat, sediment and surrounding soil are likely to be the key reservoirs involved in P cycling in these systems. The apparent difference in P availability in coastal and inland sites may mean that biological demand will affect the distribution of P throughout the ecosystem differently also. This thesis will characterise P abundance in both coastal and inland meltwater ponds, measuring P content and speciation in the key reservoirs.

1.3.2 What are the sources of P to meltwater ponds?

The main natural sources of P to temperate lake systems are catchment runoff and precipitation (Berner, 1996). In Antarctic meltwater ponds however, precipitation occurs almost exclusively as snow, and catchment runoff is from snow and ice melt, which reduces the potential for sediment loading to ponds in flood events. Furthermore, the low temperatures and arid conditions typical of Antarctic systems can also reduce rates of some geochemical and biological weathering processes in catchment soils (Campbell & Claridge 1987, Bate *et al.* 2008). Therefore, the major sources of P to Antarctic meltwater ponds may be different. Potential sources of P to ponds may include precipitation and runoff, as well as leaching of soils and sediments, and introduction of seabird guano, aerosols and windblown material (Fig. 1.1).

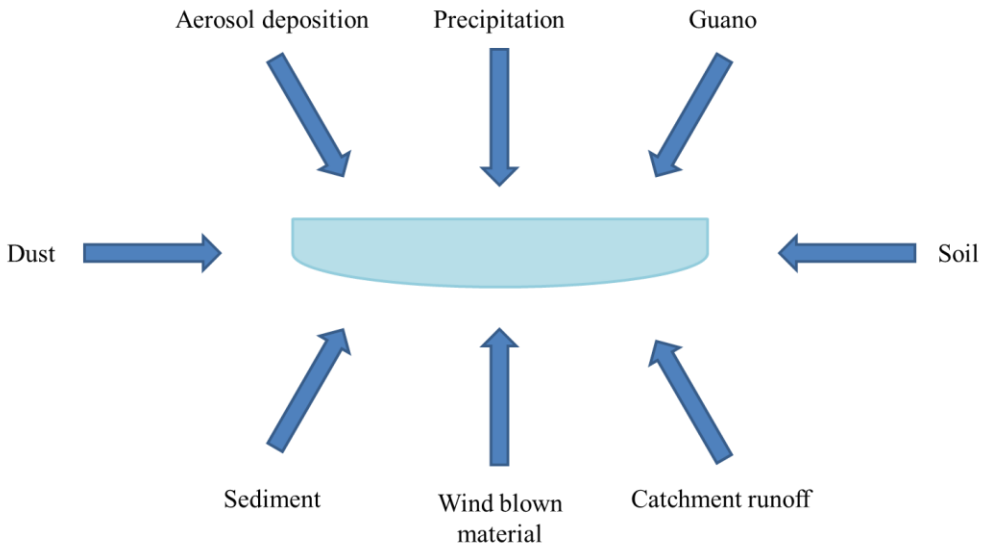


Fig. 1.2 Summary of potential sources of P to meltwater ponds.

Chemical weathering has been suggested to occur very slowly in Antarctic soils (Campbell & Claridge 1987), however seems to occur faster in stream beds. Chemical weathering in streams of the Lake Fryxell Basin, Taylor Valley was measured by H_4SiO_4 and HCO_3^- fluxes, and shown to occur at rates comparable to temperate systems (Lyons *et al.* 1997). The exposure to freeze thaw cycles, steep temperature gradients and wetting and drying cycles were proposed as factors which may accelerate the weathering process (Colman & Dethier 1986, Lyons *et al.* 1997). Studies have shown that melt stream sediments in the McMurdo Dry Valleys act as a significant nutrient source for early season stream flows, suggested to be a result of rock weathering or salt concentration as the river dries and freezes during winter (Weand *et al.* 1977, Torii *et al.* 1988, Howard-Williams *et al.* 1997). Bate *et al.* (2008) showed that stream sediment from the Taylor Valley contained 40 % less P than adjacent soils, also suggesting that sediments act as a P source to streams.

In another study on lakes, Kaup and Burgess (2002) investigated nutrient concentrations in surface and subsurface meltwater flows to lakes in the Larsemann Hills, Antarctica. Surface inputs had 13 – 30 µg DRP L^{-1}, while subsurface flows had a much higher range of 36 – 173 µg DRP L^{-1} (Kaup & Burgess 2002). Nitrogen showed similar trends with NH_4^+ and NO_3^- being substantially more concentrated in the subsurface waters. Contrary to the findings in Dry Valleys studies, this study showed increasing concentrations of nutrients at the end of summer (Kaup & Burgess 2002).

Pond soils and sediments have not yet been studied as potential P sources, and no quantities or fluxes of P into ponds have been identified. This thesis will use the speciation of P in pond reservoirs and the differences between soil and sediment reservoirs to identify if soils and sediments have a role as a P source to meltwater ponds. The role of snow, seabird guano, and dust as P sources will also be explored.

1.3.3 Is P distribution site specific, or can models of a particular inland and coastal system be applied elsewhere?

There is an established pattern of meltwater ponds typically having high N:P ratios in inland areas, and low N:P ratios near the coast. In Dry Valley soils, landscape history has had an influence over soil and stream sediment P content (Bate *et al.* 2008). Glacial tills in particular appeared to impose a geological legacy on the ecosystems, influencing soil biogeochemistry, and that of streams. It is likely that the geology of a pond's catchment will limit the amount of P that is able to partake in the ponds P cycle, particularly if there is no substantial aerosol input to the catchment. It is possible that similar processes occurring in ponds drive similar P behavior in inland and costal environments, but that increased biological demand in P-limited systems may lead to more significant differences in P distribution. This thesis will use an example of a coastal and an inland system to create a model for P distribution in each, and test the model against P characterization at several other pond sites, both in coastal and inland areas. The results will establish if P distribution is different for coastal and inland systems, and if it can be predicted for coastal and inland systems in different locations. This will also determine whether local geology, distance from the coast, or in pond processes drive P content and distribution.

1.3.4 What processes regulate P mobility in these environments?

In meltwater systems generally, a number of biological, chemical and physical processes have been shown to affect P. Biological uptake rates for P have been measured (Vincent & Vincent 1982), P release from benthic mats has been observed in freeze-thaw cycles (Howard-Williams *et al.* 1997, Hawes & Howard-Williams 1998), alkaline phosphatase enzyme activity has been measured (Dore & Priscu 2001), and cryoconcentration of P has been observed during winter freezing of ponds (Wait 2011). Additionally, high summer pH and reducing conditions have been measured in ponds (Healy *et al.* 2006, Wait *et al.* 2006, Wait *et al.* 2009), which are likely to impact on any P associated with metal oxides (Cornell & Schwertmann 2003).

Many of these processes have not been quantified to determine their importance for P transfer to/from, or within ponds, nor have fluxes of P been identified. This thesis will address biological uptake of P, and use speciation in soils and sediments to better understand P transfer processes that occur in meltwater ponds.

1.4 Thesis outline

This thesis consists of seven chapters, four of which address the research questions. These four chapters (Chapters 3, 4, 5 and 6) contain a brief introduction to the questions and themes that will be addressed.

- Chapter 2 – Methods

  A description of the field, analytical and modeling methods used to produce this research. The sampling locations are also presented.
- Chapter 3 - Characterisation of P distribution in ponds near Bratina Island, on the McMurdo Ice Shelf

  This chapter addresses research questions 1.3.1 and 1.3.2, evaluating P abundance and sources in ponds at the coastal location of Bratina Island on the McMurdo Ice Shelf. A conceptual model of P distribution in a coastal meltwater pond is developed.
- Chapter 4 - P distribution in inland ponds of the Labyrinth, Upper Wright Valley

  This chapter also addresses questions 1.3.1 and 1.3.2, and investigates the abundance and sources of P to inland meltwater systems in the Labyrinth of the Upper Wright Valley. A conceptual model of P distribution in inland meltwater systems is then presented.
- Chapter 5 - P distribution in other key ponds of the Victoria Land region, Antarctica

  This chapter addresses the first two research questions for a variety of coastal and intermediate meltwater systems, and validates the models constructed in chapters 3 and 4.
- Chapter 6 - Factors driving P distribution and transfer in ponds

  This chapter addresses research questions 1.3.3 and 1.3.4. The processes that transfer DRP to and from the water column in meltwater ponds are identified and quantified. Then a discussion of the results presented in this thesis interprets the impact of location on P distribution in meltwater ponds.
- Chapter 7 – Conclusions

This chapter presents the major research outcomes from this work, and makes suggestions for further investigation.

Chapter 2:
Methods

Fig. 2.1 Morepork Pond in the Miers Valley, with apparatus to sample a vertical profile of the water column, and perform the 24 hour monitoring set up at each end of the pond.

2.1 Sampling locations

Meltwater ponds from 7 areas in the Ross Dependency were sampled to contribute to this study (Fig. 2.1, 2.2). These were the ablation region of the McMurdo Iceshelf near Bratina Island, the Western end of the Wright Valley, referred to herein as the 'Upper Wright Valley', the Eastern end or the 'Lower Wright Valley', the mouth of the Miers Valley, and several locations on Ross Island, including Cape Royds, Cape Evans, Hut Point and Observation Hill. Table 2.1 shows the dates that fieldwork was completed at each site. These locations were selected to give a broad picture of P dynamics in a range of Antarctic ponds. The locations span a variety of distances from the coast, and elevations. There are also several different main lithologies in the study areas, and two sites include ponds on ice cored terrain, whilst the other sites are rock based. Each area and the ponds sampled there will be described in detail in the following chapters. Ponds at each site were selected on the basis of the following criteria: a range of the conductivities representing the span of the ponds surveyed in each location, having closed basins at the time they were first sampled, and where possible ponds with dimensions less than 25 m were sampled. Pond names used in this thesis are not recognized in the Gazetteer of Antarctic Place Names. Hence latitude and longitude information is provided for each pond.

Table 2.1 Pond sampling locations and the dates on which they were sampled.

Location	Dates visited
Bratina Island	15th January 2011, 27th January 2012, 14-21 January 2013
Cape Royds	3-10th January 2011
Cape Evans	17th January 2011
Upper Wright Valley	7-13th January 2012
Lower Wight Valley	14-21st January 2012
Hutt Point and Observation Hill	25th January 2012
Miers Valley Mouth	21-28th January 2013

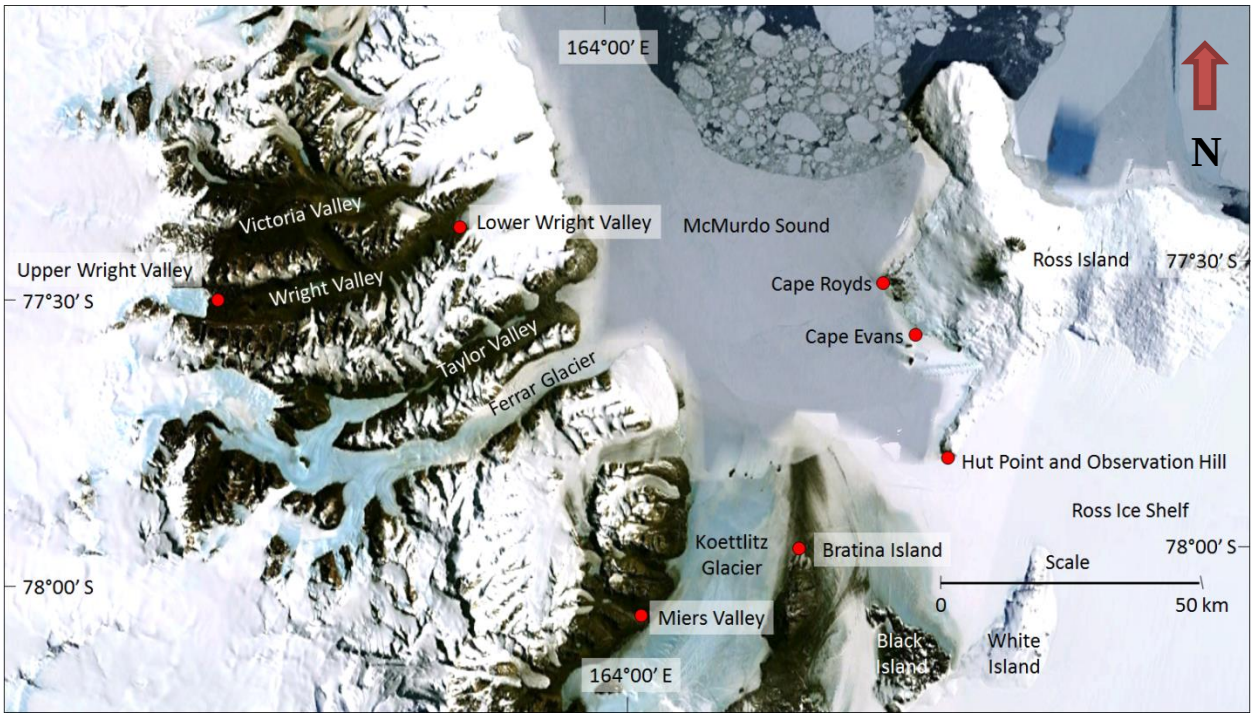


Fig. 2.2 Sampling locations in the Ross Dependency. Sample sites are denoted by a red marker, and key geographical features are marked. Image taken from Google Earth July 2014.

2.2 Sampling methods

The field methods and sample collection varied slightly from year to year, as more was learned about the previous systems sampled, and new questions formed. Table 2.2 displays the sampling undertaken at each sample site.

For all ponds, size, depth, mat cover and characteristics, presence of pond surface ice and visible soil salts, as well as any catchment features were recorded. Temperature, pH, dissolved oxygen (DO) and conductivity were measured *in situ* using a recently calibrated HACH HQ40D meter. Maximum pond depth was measured where possible, or visually estimated based on prior measurements, and at Bratina Island, shoreline markers at the pond edges.

All sampling containers were new, clean and sterile, or had been acid washed and deionised water rinsed. All containers and sampling equipment for water were rinsed 3 times with pond water prior to taking samples. Water samples for major ion analysis were collected unfiltered into 50 mL polypropylene centrifuge tubes, or into glass vials containing 0.2 mL phosphoric acid (for DIC), and kept refrigerated until analysis. The samples for DIC were the first sample taken,

when the pond surface had been minimally disturbed. Water samples for nutrient analysis were collected directly into 1 L polyethylene bottles, then filtered through acid-washed Whatman GF/F filters, within 4 hours of collection for 2013 samples, and within 24 hours of collection for 2011 samples. Filtrate was collected for dissolved N and P species analysis, and the GF/F filter was collected for particulate N and P analysis. Particulates were also collected onto a precombusted Whatman GF/F filter for particulate C and N analysis, and onto an untreated Whatman GF/F filter for chlorophyll a (Chl a) analysis. All nutrient samples were frozen as soon as possible, and always within 24 hours of collection.

Table 2.2 A summary of the sampling and experimental methods (as explained in this chapter) used at each sample site.

	Bratina Island		Cape Royds	Cape Evans	Hut Point	Upper Wright	Lower Wright	Miers Valley
	2011	2013						
Pond survey	x	x	x	x	x	x	x	x
Water sampling	x	x	x	x	x	x	x	x
Soil sampling	x	x	x	x	x	x	x	x
Sediment sampling		x			x	x	x	x
Microcosm uptake		x				x		x
In situ uptake		x						x
24 hour monitoring		x						x

Cores of microbial mat (5 per pond except for at Bratina Island in 2013, when only 3 per pond were taken, all of 1 cm diameter) were collected using a cut-off syringe, and placed into glass scintillation vials, then frozen within 12 hours. Cores were taken to the mat-sediment interface, thus core depth varied with microbial mat thickness. Soils were sieved and the <2 mm fraction collected into polyethylene containers or 50 mL polypropylene centrifuge tubes, and stored at 4 °C in the dark. Soil salts were collected from visible encrustations into 15 mL polypropylene centrifuge tubes.

Sediment cores were taken using either; a perspex cylinder and sectioned into 1 cm slices, which were collected into polypropylene containers then stored frozen, or small cores were taken in 60 mL cut off syringes, which were then corked with a rubber bung and frozen. The ability to take cores varied with substrate, and sediment cores ranged from 5 – 20 cm depth. After return to

New Zealand, sediments were thawed, syringe cores were sectioned into 1 cm slices, and pore waters were separated by centrifuging sediments at 4000 rpm for 1 hour, prior to performing P sequential extractions. Porewaters were collected and diluted to 10 mL before filtering through a 0.45 µm cellulose acetate membrane filter, with the filtrate then re-frozen for later DRP analysis.

At several of the sample sites, two uptake experiments were performed to measure the rate of DRP uptake by the microbial mat and plankton in the system. A microcosm uptake experiment, and an *in situ* uptake experiment. Three study ponds were selected from each site where this was run. Six cores of microbial mat were collected from each pond, as well as 4 L of pond water. Each mat core was placed into a 'microcosm' 750 mL polyethylene tub, with 500 mL of the pond water, and seventh tub contained pond water without mat present (Fig. 2.3). Three of the tubs and the control were spiked with 1 mL of 25 mg P/L solution to increase the water DRP concentration by 50 µg/L. The remaining 3 tubs were spiked with 0.1 mL of the solution, to increase the water DRP by 5 µg/L. The tubs were all insulated in a pond near to the field camp, which regulated temperature and environmental conditions. At time intervals of 15 minutes, 1 hour, 2 hours, 4 hours, 8 hours and 24 hours a 50 mL aliquot of the overlying water was removed and filtered into a 50 mL polypropylene centrifuge tube. Aliquot samples were frozen within 12 hours for return to New Zealand. For the experiment that was run in the Upper Wright Valley a number of samples partially froze during the overnight incubation. For these the volume of liquid in the tub was measured, and the sample taken from the liquid.

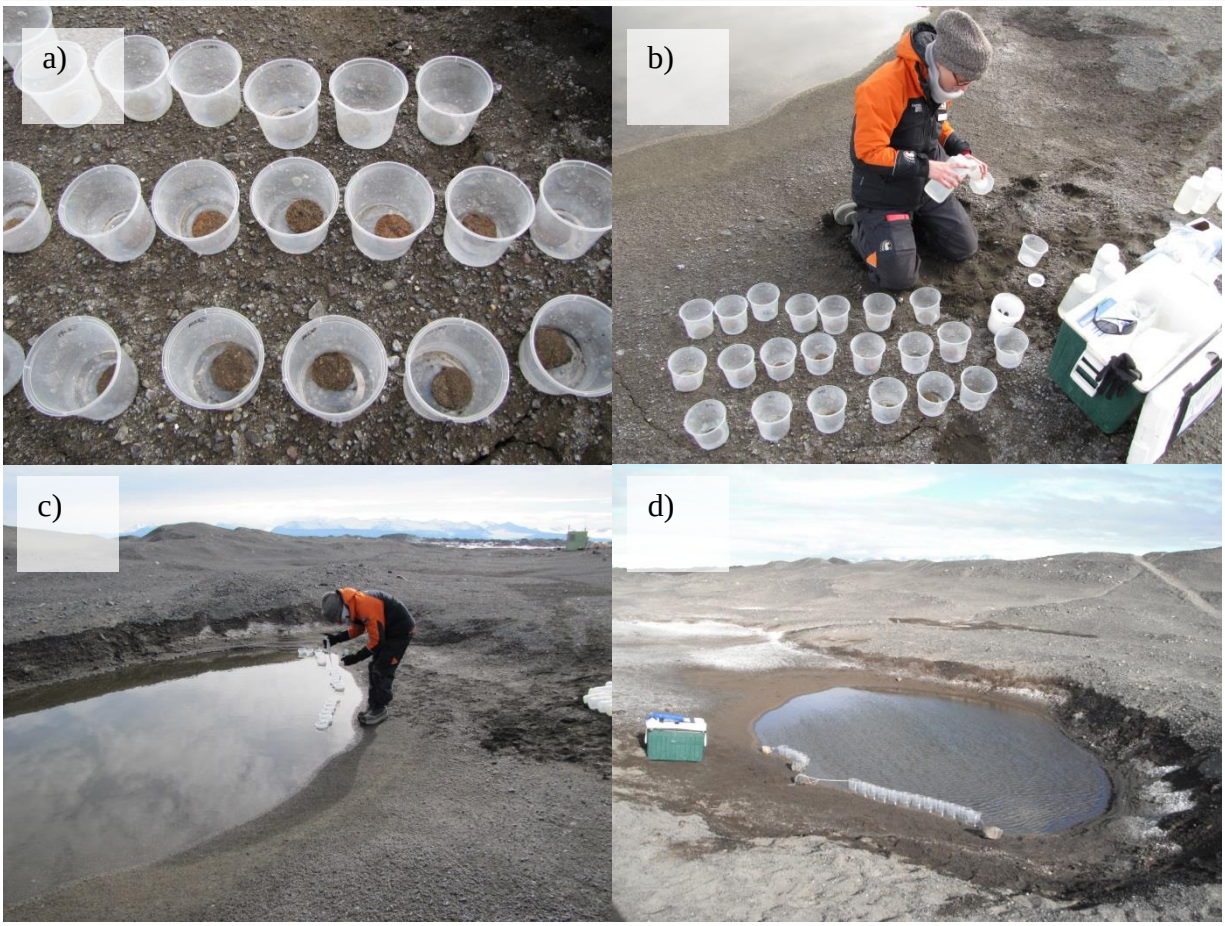


Fig. 2.3 Uptake experiments at Bratina Island. a) mat cores are placed in polyethylene tubs, b) 500 mL of collected pond water is added, c) the tubs are spiked with K_H2PO_4 solution, and d) tubs are incubated in Camp Pond for the duration of the experiment

A second *in situ* uptake experiment was performed only at Bratina Island and in the Miers Valley, which isolated a small section of the pond water and mat. Four 1 L bowls, two transparent and two opaque black were allowed to fill with pond water and were inverted over a section of mat (Fig. 2.4). Care was taken to have all bowls overlying sections of mat that were visually similar to the majority of the ponds mat, and all bowls were placed at the same depth. The bowls had rubber tubing from inside the bowl to a syringe, which allowed sampling from the water within the bowl. Syringes were left attached to the tubing during the time monitored, and a volume equivalent to the tube volume of water was expelled prior to sample collection. A second tube was placed in the bowl opposite the syringe tube to allow inflow of water whilst extracting the sample. Having this inflow on the opposite side of the outflow was intended to minimise the amount of water from outside the bowl that was sampled .A 50 mL water sample was taken at time zero as the bowls were set up, and another was taken after the bowls had been sitting on the

pond floor for 48 hours. Samples were filtered immediately and frozen for analysis once returned to New Zealand. Small rocks were placed on the bowls to prevent them floating, which along with the syringes cast some shadow on the mats beneath the transparent bowls.

Fig. 2.4 The bowl uptake experiment in Finch Pond in the Miers Valley.

Two ponds each at Bratina Island and in the Miers Valley were selected for a much more intensive soil sampling. Soil samples were taken from 4 perpendicular transects from the pond edges, toward the edge of the pond catchment for up to 22m. Sampling was performed every meter in the 4 – 5 m from the pond edge, and every 2 to 4 m thereafter.

At Bratina Island, and at Cape Royds some soils were visibly affected by seabird guano. One sample of guano affected soil was collected at Cape Royds, and at Bratina Island four soil samples visibly affected by skua guano were taken, as well as four control samples immediately adjacent to the guano-affected soil.

At Bratina Island two ponds were selected to study for dust accumulation. Two dust collectors were placed at each pond on the 15/01/2013 and collected on the 1/02/2013. The collectors consisted of acid washed plastic aerofoil shaped discs 265 mm in diameter, which were filled with acid washed glass balls to prevent dust leaving the discs, and were electrically grounded to the permafrost to prevent static charge build up. The dust and glass balls from each disc were collected into plastic bags, and dust was separated and collected onto filter papers using 50 mL of deionized water to rinse the glass balls. One collector at Skua pond also accumulated snow melt, which was separated and used for rinsing the glass balls instead of deionized water. The snow melt was analysed by the same methods followed for water samples. Dust samples were analysed for labile P.

Fig. 2.5 Assembling a dust collector in the field.

At Bratina Island some smaller ponds were selected to measure detailed bathymetry, determined using a weighted, calibrated line. At Bratina Island and in the Miers Valley, depth to the permafrost ice in the soil was measured around ponds, either by digging to locate the ice level, or driving a metal stake into the soil or pond sediment until the ice was reached (Fig. 2.6). Soil pits were dug around the ponds and visible changes in moisture content were recorded in the soil

profile as; water-saturated soil (where water seeped from the soil into the pit), visibly moist soil, dry soil, or ice cemented soil (permafrost).

Fig. 2.6 A soil pit dug at Canary Pond in the Miers Valley, showing the ice cement below the active layer.

Two ponds at Bratina Island and one pond in the Miers Valley were selected for 'short term monitoring'. Each pond was monitored for an 8-24 hour time period, to gauge possible effects of the diurnal cycle on pond P. Each hour the temperature, pH and concentration of dissolved oxygen were measured both at the pond surface, and 2-3 m from the pond edge, approximately 5 cm above the microbial mat (Fig. 2.7). A sample was also taken, filtered and frozen for DRP analysis.

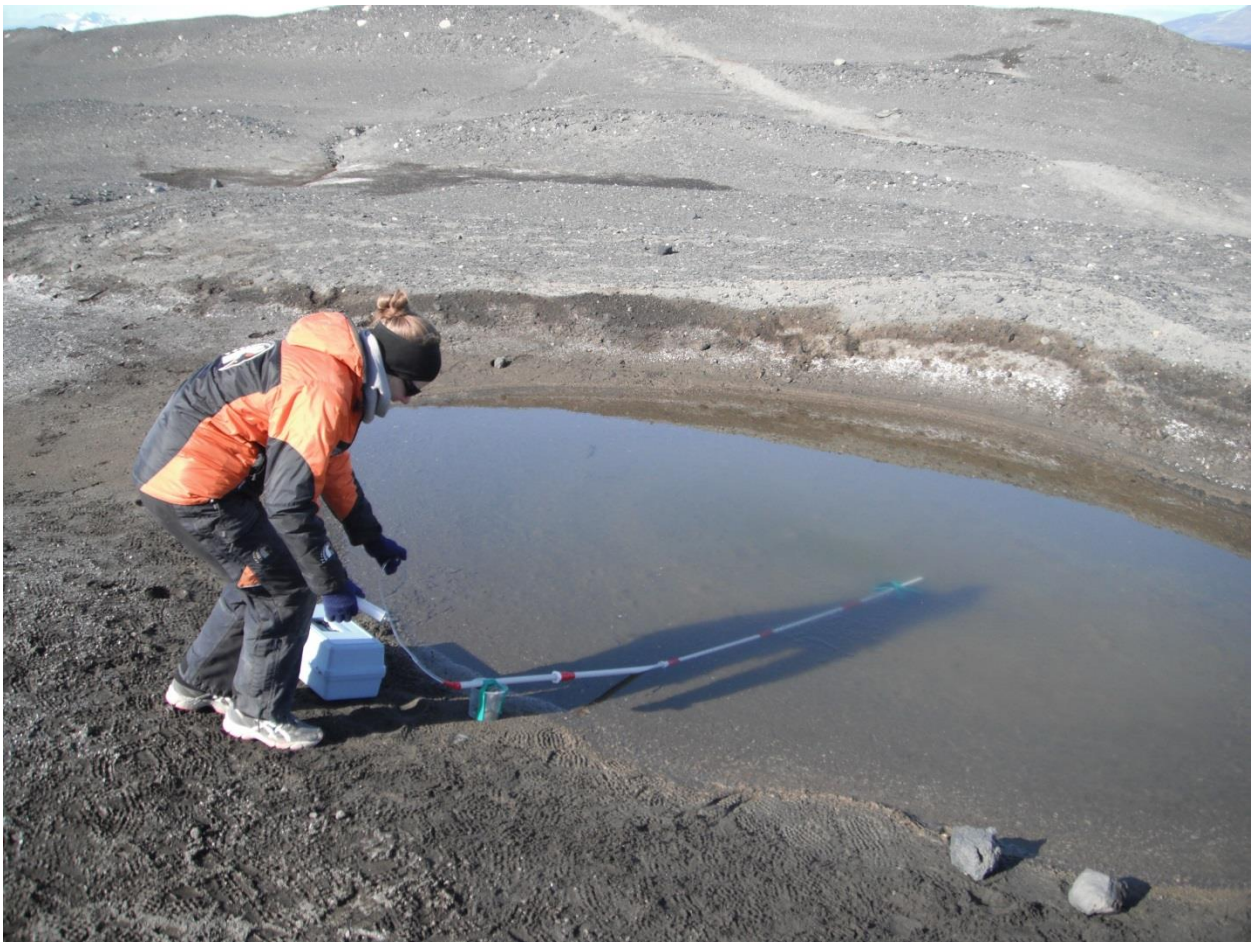


Fig. 2.7 Sampling the base of Camp Pond at Bratina Island to perform the 24 hour monitoring on pond bottom water.

2.3 Analytical methods

Water samples were analysed for DRP, using either an Astoria autoanalyser with a detection limit of 1 µg/L, or ascorbic acid colourimetry (APHA Method 4500) and a HACH 3900 spectrometer, with a detection limit of 2 µg/L. Total dissolved phosphorus (TDP) was analysed after a persulphate digestion to convert all P to DRP, and dissolved organic phosphorus (DOP) calculated by difference. Total P (TP) was measured on persulfate digests of unfiltered water samples, or was calculated from a sum of the TDP and PP concentrations. NO_3-N and NH_4-N were analysed for 2011 samples on an Astoria autoanalyser with a detection limit of 1 µg/L, these values have been added and are referred to as TIN, total inorganic nitrogen. PP was determined after acid persulfate digestion of the filter paper, with a detection limit of 0.1 µg/L.

Chl a was analysed flourometrically after grinding the filter paper in 95 % acetone, as described in Hawes et al (2011).

Water samples were analysed for dissolved inorganic carbon (DIC) using an infra-red gas analyser, as in Hawes et al. (2011). Concentrations of HCO_3 were calculated from the DIC concentrations, as the second dissociation constant of carbonic acid is 10.33, and only one pond exceeded this, HCO_3 will be the dominant carbonate ion in the pH 8.7 – 10.38 range measured in the ponds. Unfiltered water samples were analysed for Na, K, Ca and Mg by HPIC (high performance ion chromatography) with detection limits of 1 µg/L for Mg, 3 µg/L for Ca, 5 µg/L for Na and 80 µg/L for K. The charge balance for the major ions was always within 10%, and usually within 5%.

Soils and sediments were analysed for "Total P" by boiling 0.5 g of sample in 10 mL concentrated nitric acid until near dryness, followed by boiling in 10 mL of 10 % nitric acid for 2 hours. The mixture was diluted to 50 mL and analysed for DRP as in water samples. This method does not dissolve silicates, and therefore any residual P incorporated in silicate minerals has not been addressed in this study. This procedure recovered 89 % of the total P of the PACS-2 certified reference material.

Soil "Labile P" concentrations were determined by extraction of 10 g of soil in 50 mL of 0.5 M $NaHCO_3$, followed DRP analysis. Soil moisture was determined gravimetrically after drying a sample overnight at 105 ºC. Mass loss on ignition (LoI) was then measured after heating the sample at 450 ºC for three hours. Soil pH was measured on a 10 g sample mixed in 20 mL of deionised water for 1 hour. 30 mL of water was then added to this slurry, and shaken for another hour before conductivity was measured on the same solution.

The mineralogy of soil salts was identified using energy dispersive spectrometry (EDS) on an environmental scanning electron microscopy (ESEM). This also enabled P concentration in the salts to be measured to a detection limit of approximately 1 atomic percent. One soil and one sediment sample from Fogghorne Pond at Bratina Island were analysed for crystalline mineralogy by XRD.

Soils from the transect samples at Bratina Island and the Miers Valley were analysed for pH and conductivity on a 1:2, and 1:5 slurry of sediment to DI water respectfully. Soil moisture was

determined gravimetrically on a 10 g sample after drying for 24 hours at 105 °C. Soil mass loss on ignition (LOI) was determined gravimetrically on the dried moisture sample, after placing in a furnace at 450 °C for 3 hours.

2.4 Sequential Extraction procedures

Two sequential extraction procedures were selected for use in this study. A four step Psenner type sequential fractionation procedure (Psenner *et al.* 1988, Rydin 2000) was used to determine P fractionation in sediments, and in some of the soils to compare with these sediments. This extraction was selected to target reactive phases of P that may be released during environmental conditions that may develop in the pond sediments. This included an 'exchangeable P' phase that can be released via ion exchange at the sediment-water interface, a 'reducible oxide-bound P' phase, which will become soluble when reducing conditions develop in sediments, and a 'metal oxide adsorbed and organic P' phase, which may be released from sediments during high pH conditions. The Psenner method identifies four different P fractions, based on the speciation of P in the sediment. Sediment (1 g) was mixed end-over-end in 50 mL of the following reagents for the specified time, to target each P fraction:

1. 1 M NH_4Cl for 2 hours to release "Exchangeable P"
2. 0.11 M $NaHCO_3$ and $Na_2S_2O_8$for 1 hour, to release "Reducible oxide-bound P" (RO-P)
3. 0.1 M NaOH for 16 hours, to release "Metal oxide adsorbed/Organic P" (MO-P)
4. 0.5 M HCl for 16 hours to release residual P, henceforth referred to as "Apatite P"

After each step the mixture was centrifuged for 15 min at 4000 rpm and the supernatant collected for analysis. The NH_4Cl, NaOH and HCl extracts were analysed by spectrometry, while the BD extracts were analysed by ICP-OES.

A modified version of the Hedley sequential fractionation procedure (Hedley *et al.* 1982, Lajtha *et al.* 1999) was used to determine the P fractionation in soils. This extraction was selected to give a greater indication of the chemical speciation of P present in soils than is afforded by the Psenner extraction method, and to identify a 'soluble P' fraction that may be released when soils interact with fresh snow melt. Modified Hedley fractionations have also been successfully utilized to determine P fractionation in McMurdo Dry Valley soils (Bate *et al.* 2008). The

method identifies four different P fractions, by mixing 0.5 g of soil with 30 mL of each reagent for 18 hours, as follows:

2. Deionised water, to release “Soluble P”
3. 0.5 M $NaHCO_3$, to release “Labile P” sorbed on soil surfaces
3. 0.1 M NaOH, then a further extraction in 0.1 M NaOH after placing for 5 minutes in an ultrasonic bath, to release “Metal oxide adsorbed/Organic P” (MO-P) from readily reactive surfaces, and from surfaces exposed by particulate disaggregation respectively. The two extracts were analysed separately and the results added to determine the “Metal oxide adsorbed/Organic P” (MO-P) for this extraction.
4. 1.0 M HCl, to release the residual P, henceforth referred to as ‘”Apatite P’

After each step the mixture was centrifuged for 15 min at 4000 rpm and the supernatant collected for analysis by spectrometry. For the RO-P fraction of the Psenner extraction, analysis was performed on a 1:10 dilution of the extract, which had been carried through the same persulfate digestion that was performed on DOP samples described previously. This step prevented formation of sulfur and metal sulfides in the analysis procedure. For both procedures, ‘reactive P’ combines P removed in steps 1-3.

Table 2.3 Summary of the terminology used for soil and sediment P fractions in this thesis, and the extraction method, and the interpreted form of P they refer to. The soil labile P used a 1:5 soil:extractant, the Hedley extraction used 1:30, and the Psenner extraction 1:50.

Term	Extraction	P form/speciation
Soils only		
Labile P	0.5 M HCO_3 for one hour	P that is soluble or easily released by ion exchange. Deemed bioavailable.
Soluble P	DI water for 16 hours	Soluble P. Deemed bioavailable.
Hedley Labile P	0.5 M HCO3 for 16 hours	P loosely sorbed to soil surfaces, releasable by ion exchange. Deemed bioavailable.
Hedley MO-P	0.1 M NaOH for 16 hours, further extraction of 0.1 M NaOH for 16 hours after sonication	P sorbed to metal oxides and organic P. May become bioavailable under high pH or reducing conditions.
Hedley 'Apatite P'	1.0 M HCl for 16 hours	P associated with calcium, any apatite, and P associated with other acid soluble minerals. Requires weathering to be made bioavailable.
Sediments (and some soils for comparison)		
Exchangeable P	Psenner extraction of 1:50 sediment : 1 M NH4Cl for two hours	P loosely sorbed to surfaces, releasable by ion exchange. Deemed bioavailable.
RO - P	Psenner extraction of 1:50 sediment : 0.11 M NaHCO3/Na2S2O8 for one hour	P sorbed to reducible metal oxides. May become bioavailable under high pH or reducing conditions.
Psenner MO-P	Psenner extraction of 1:50 sediment : 0.1 M NaOH for 16 hours	P sorbed to metal oxides. May become bioavailable under high pH conditions.
Psenner 'Apatite P'	Psenner extraction of 1:50 sediment : 0.5 M HCl for 16 hours	P associated with calcium, any apatite, and P associated with other acid soluble minerals. Requires weathering to be made bioavailable.

2.5 Calculations and modelling

Reservoir size was calculated from pond size and structure data, and P concentrations. Pond shapes were simplified into elliptical cones, and their volume, surface area, and pond floor area were derived on this basis. The sediment reservoir was considered to extend to the ice cemented layer, for the average depth for the area, and included the water-saturated substrate below the pond water level. The zone of saturated soil was defined as saturated substrate above the pond

water level, and reservoir volume was calculated using the geometry of this zone at P70 Pond at Bratina Island. The area of the saturated – moist soil boundary was integrated from 39 cm above pond level at the saturated zone edge, 1.6 m laterally from the pond, to the water level at the pond edge to give a volume, from which the volume of the ice cement, calculated in a similar manner was subtracted. A density of 1.5 g/mL was used for calculations of sediment and soil P (McLeod *et al.* 2009). Microbial mat volume was estimated from the pond floor area, and the mat thickness in each pond.

2.6 Quality assurance and error estimation

2.6.1 Data integrity

Meters for field and lab measurements were calibrated frequently, and checked daily on standard solutions.

For all chemical analyses, standard and blanks were run prior to any analysis. For phosphorus analytical work, separate calibrations were made for each sample matrix in sequential extractions, and were ratified each time samples were run by also analyzing standards prior to, and alongside analyses. All P analyses were verified with sample spikes to ensure good return in the variety of matrices used.

For major ion analysis, a separate calibration was performed for each batch of samples that was analysed. Calibrations and contamination were checked regularly throughout analytical work by running one standard and one blank typically after every set of 10 samples. For major ion analyses, ion balances were typically within 5 %, and always within 10 %.

Detection limits for P were determined by detecting the signal response on twenty blanks, and multiplying the standard deviation by 3. This gave a detection limit of 2 µg/L P for samples analysed in a 5 cm path length cell.

2.6.2 Uncertainty in the models

A ± 50 % error was estimated for the P content calculated for reservoirs in the models based on errors in the approximation of reservoir volume, and P concentration. The pond size measurements were estimated to be accurate to within ± 10 %, however pond shape

approximation is the major source of uncertainty. Using different geometries to calculate reservoir volumes changed the volumes by up to 30 %. Analysis of standards and certified reference materials were replicated with ± 5 % accuracy, and replicate analyses of soils and sediments were accurate to ± 10 %, likely due to sample heterogeneity. For this reason calculations of reservoir volume and P content have been given to one significant figure. The values of P content are especially sensitive to the depth of soil and sediment, and are also sensitive to the calculation method used to determine reservoir volume.

Chapter 3:
Characterisation of P distribution in ponds near Bratina Island, on the McMurdo Ice Shelf

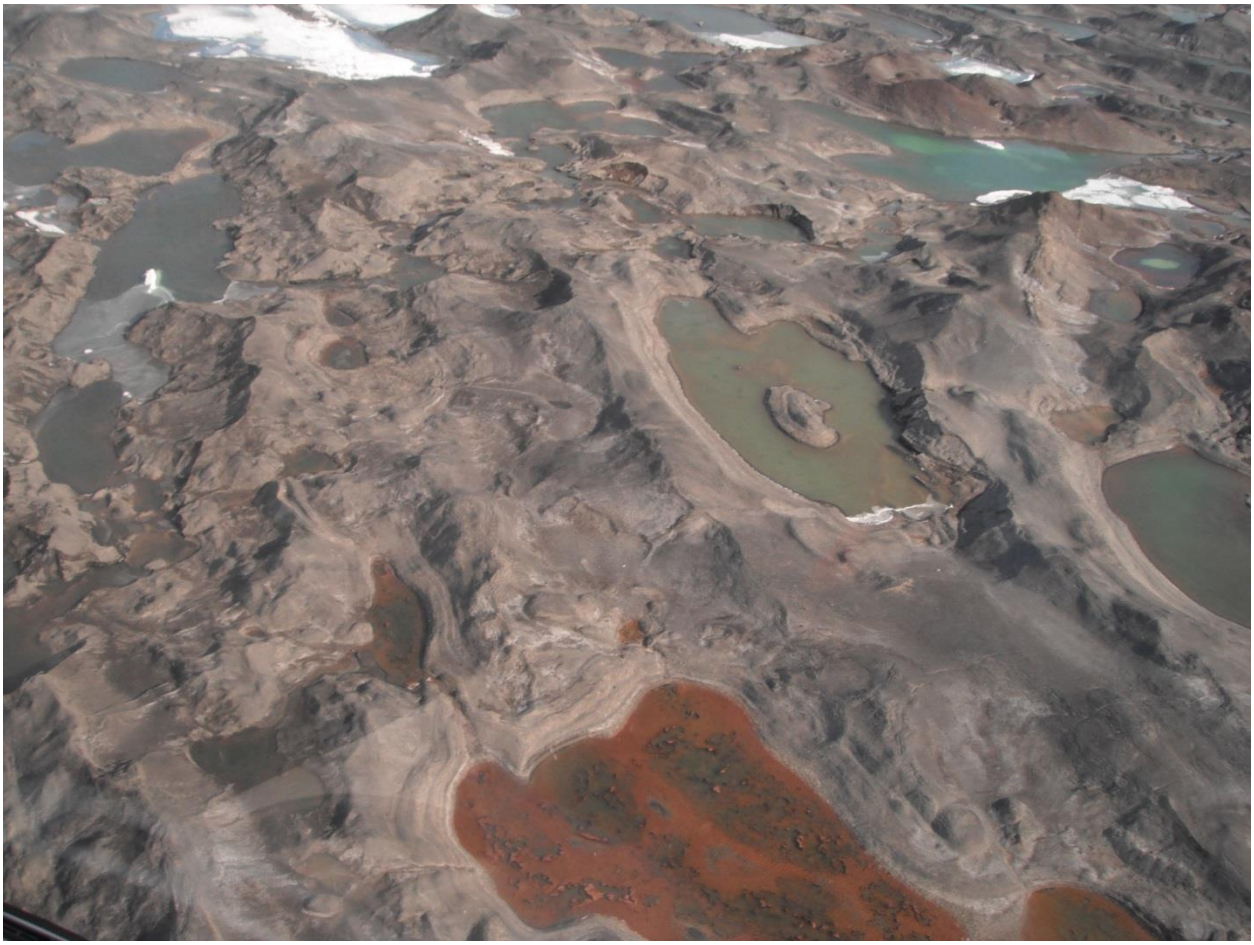


Fig. 3.1 Ponds on the McMurdo Ice Shelf near Bratina Island

3.1 Introduction

Meltwater ponds are small, terrestrial aquatic systems, which are common in the ice free areas of Antarctica. These systems are important habitats which can accumulate dense biomass relative to other cold desert ecosystems. An extensive network of meltwater ponds covers an area of 1500 km^2 on the McMurdo Ice shelf, hosting the largest concentration of terrestrial biomass in the Ross Sea region (Howard-Williams et al. 1989). Most of the ponds are closed basin systems, with snow melt thought to be the major input of water, and evaporation and sublimation the major output. The sample site represents a coastal system in which production is limited by N availability, and factors effecting N availability are reasonably well understood (Vincent & Howard-Williams 1994, Sorrell *et al.* 2013). There has been little research into the sources of P to ponds and factors affecting its release into dissolved form, and hence its bioavailability.

Contribution of this research

We have used the biogeochemical cycle concept to interpret P behavior in meltwater ponds of the McMurdo Ice Shelf. In biogeochemical cycles, elements cycle between compartments of the ecosystem (reservoirs) via abiotic and biotic processes, enter through sources and exit through sinks. In the development of a P cycle for meltwater ponds, we consider reservoirs to include the pond water itself, biomass, sediment, and the saturated marginal soil. Sources of new P to a McMurdo Ice shelf meltwater pond can be from P release from soils, proximal ice melt and seabird guano, as well as wind transport of snow-borne aerosols, foams and organic detritus.

The objectives of this chapter are to characterize P in the ponds of the McMurdo Ice Shelf, by:

- Establishing the distribution of P in the ecosystem
- Identifying the important reservoirs of P
- Determining the speciation of P in the reservoirs
- Creating a model of P distribution in ponds from this site
- Identifying the sources of P to these coastal ponds at Bratina Island

3.2 Site description

The MIS is a portion of the Ross Ice Shelf that lies between Brown Peninsula, Minna Bluff, White Island, Black Island and Ross Island, with its northern edge meeting the Ross Sea (Fig.

3.2). The MIS is an ablation zone, and the ice shelf is nourished by bottom freezing of seawater. The area in the ablation zone moves slowly, which together with ablation rates of up to 441 mm during summer, concentrates debris on the surface (Glasser *et al.* 2006). Debris cover on the ice shelf is not uniform, and two types of surface topography have been defined: dynamic, sparsely covered "pinnacle ice" which has melt streams and pools in a surface relief of 1-2 m, and "undulating ice" (Howard-Williams *et al.* 1989). Undulating ice is overlain by > 100 mm of debris, and is stable. A surface relief of ca. 10 m has led to the formation of hundreds of sediment lined, long lived meltwater ponds on the ice cored terrain. The undulating ice occurs in the area between Bratina Island, a volcanic cone that penetrated the ice shelf, and Brown Peninsula. Debris around Bratina Island is thought to include the debris load delivered by ice movement during the last glacial maximum, in addition to marine sediments and faunal remains entrained during bottom freezing, and transported to the surface via ablation (Glasser *et al.* 2006).

The meltwater ponds near Bratina Island range from <10 to >100 m^2 in size, and display a range of physical traits and chemical compositions (Wait *et al.* 2006). The majority of ponds thaw entirely each summer, however some remain permanently ice covered. The ponds are approximately 30 km from the ice shelf edge and the Ross Sea. The prevailing major ion chemistry for the area's ponds is Na – Cl dominated (Webster-Brown *et al.* 2012), however some ponds are sodium sulphate dominated (Wait *et al.* 2006). Conductivities range from <0.1 to > 50 $mScm^{-1}$, and pond pH can vary between years, but is generally between 9 and 10 (Hawes *et al.* 2014). Nutrient concentrations typically show N:P ratios less than the 16:1 Redfield ratio (Hawes *et al.* 2014), indicating any nutrient limitation is likely to be due to N availability. Concentrations of both DRP and DOP range from < 1 to many hundreds of µg/L (Sorrell *et al.* 2013, Hawes *et al.* 2014).

In autumn and winter ponds undergo a gradual freezing process, where a freezing front descends from the pond surface and cryoconcentrates solutes (Wait *et al.* 2009). Solutes are excluded from the ice as it forms, and a residual brine can persist at the base of ponds if mixing does not occur once the pond has thawed (Wait 2011). These ponds are called 'stratified ponds'. Wait (2011) showed in most of the stratified ponds studied, DRP and DOP behaved conservatively, however their ratio to Cl increased with depth in some ponds. This demonstrates that, in the basal brine at

the base of stratified ponds, sub-environments may form where nutrient composition is redistributed by biological processes.

The ponds accommodate vibrant microbial ecosystems that are dominated by benthic mat forming cyanobacteria (Howard-Williams *et al.* 1990). The microbial mats can grow to several centrementers thickness, and typically cover the entire pond floor. Some of the genera represented include *Nostoc sp*, *Oscillatoriales sp*, and *Leptolyngbya sp*. Photosynthesis of the mats has been suggested as a mechanism causing the high pH values measured, and can deplete inorganic carbon and nutrient concentrations (see review by Howard-Williams and Hawes, 2007). Factors influencing primary productivity are well documented (Hawes *et al.* 1993, Vincent *et al.* 1993, Sorrell *et al.* 2013), and include nitrogen availability, carbon availability, sunlight and pond age (Hawes *et al.* 1993). There are no significant seabird colonies at the island, however several breeding pairs of skua nest in the area each summer, and in 2013 one adelie penguin was observed in the sampling area on one afternoon.

3.2.1 Study ponds

Based on the selection criteria outlined in chapter 2, five ponds were selected to study (Fig. 3.2). These were Fogghorne (Fig. 3.3), Orange (Fig. 3.4), P70 (Fig. 3.5), Salt (Fig. 3.6) and Skua (Fig. 3.7), all of which have been extensively studied in previous work (Sorrell *et al.* 2013, Hawes *et al.* 2014). Skua pond is notable, as despite appearing to be a closed basin system in 2011, in 2013 it had an inflow. Skua has been documented to be part of a drainage pathway. In addition to the main study ponds, two small ponds; Huey and Son of Skua, were selected to measure detailed bathymetry. A foam that was present on the margin of Casten Pond (Fig. 3.8), some of which was observed being transported from the pond by wind, was also sampled. The ponds were not measured in 2011 for conductivity stratification due to limited time at the study site, though visual characteristics typical of stratification were not observed. In 2013 P70 was conductivity stratified.

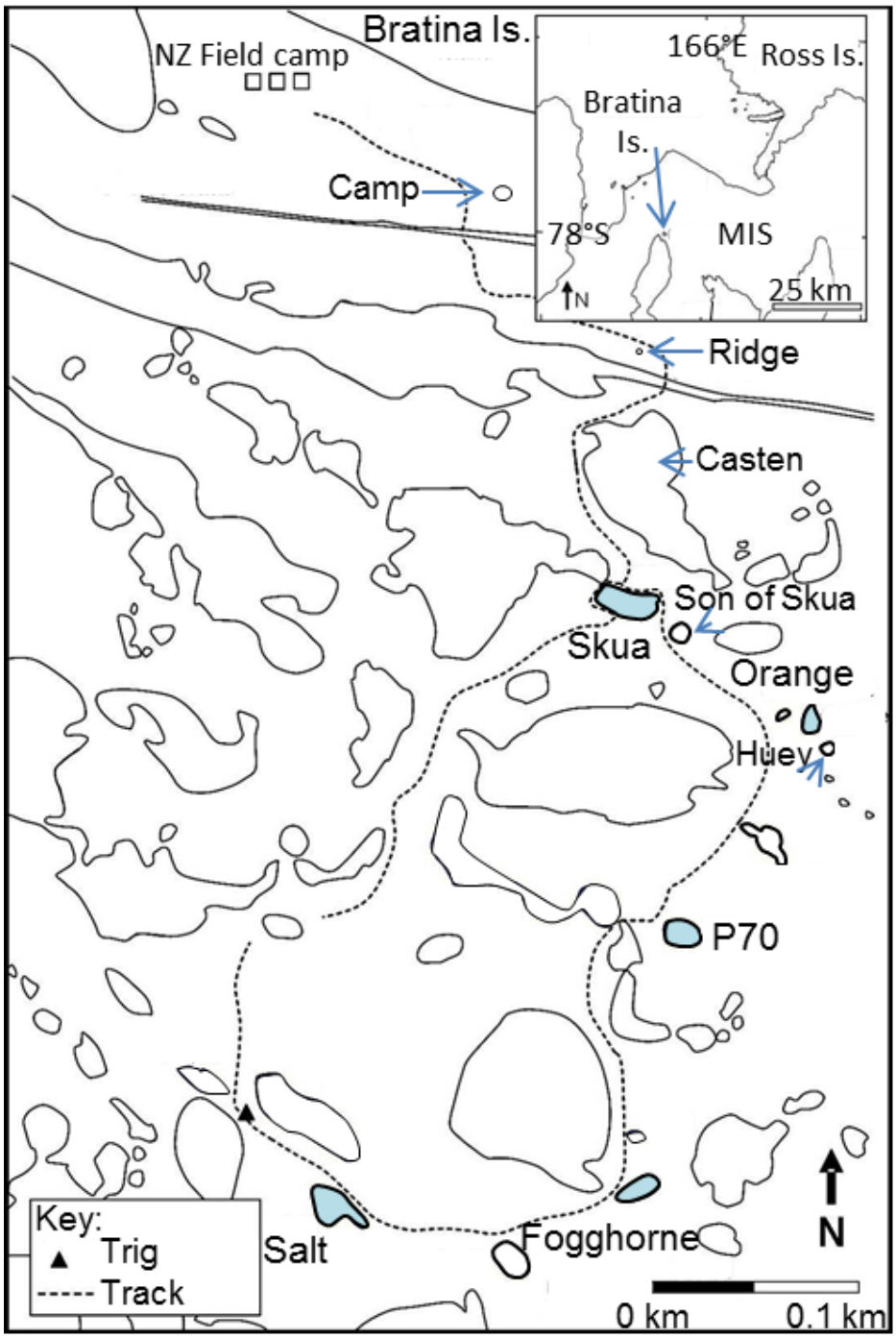


Fig. 3.2 A map of the study area at Bratina Island (modified from Wait 2011). Inset shows the location of Bratina Island on the McMurdo Ice Shelf. The study ponds are shown in blue and other named ponds are referred to in this study.

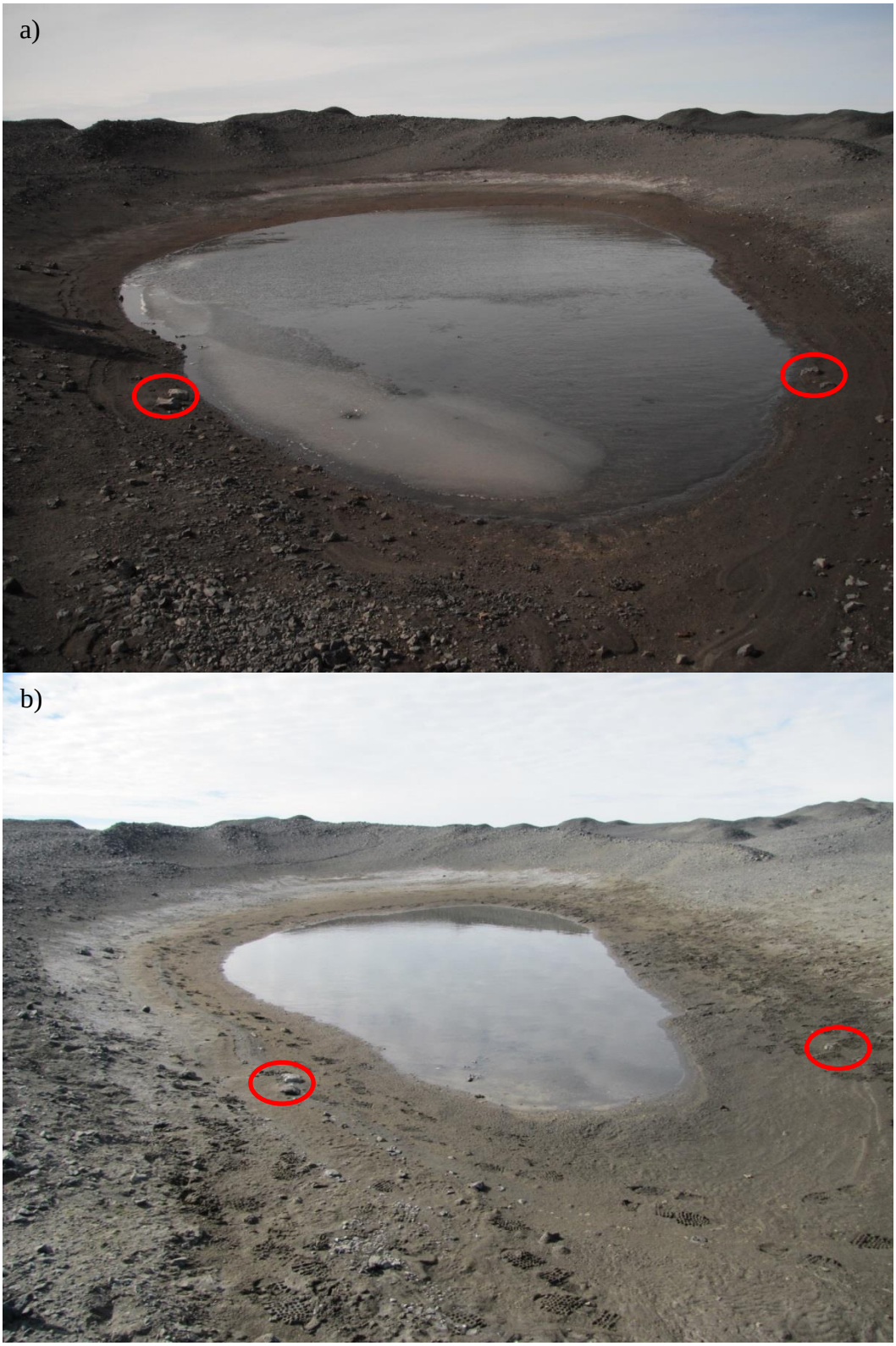


Fig. 3.3 Fogghorne Pond in a) 2011 and b) 2013. Note the drop in water level during this time. The red circles show rocks at the pond edge in 2011 are 1 – 2 m from the pond edge in 2013.

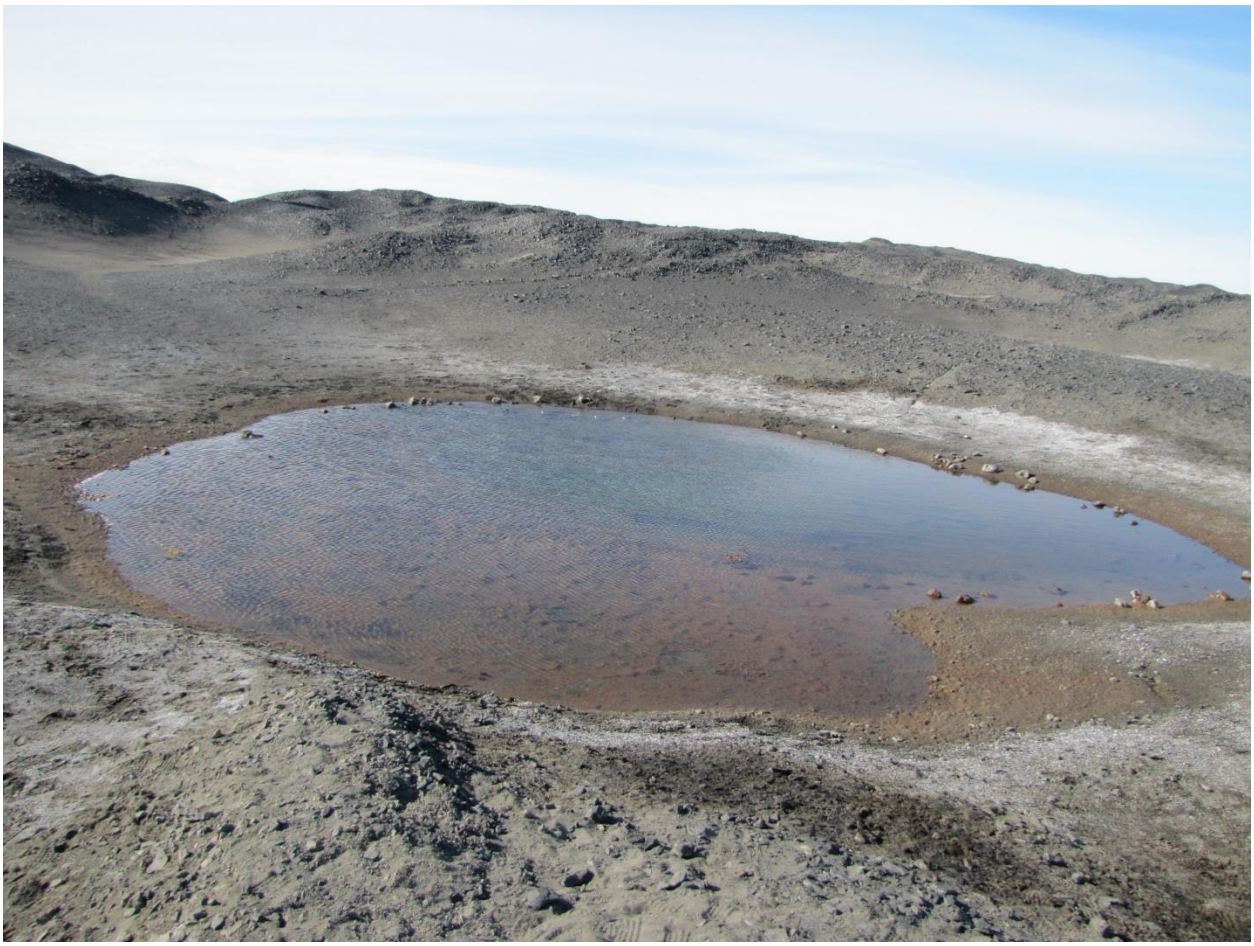


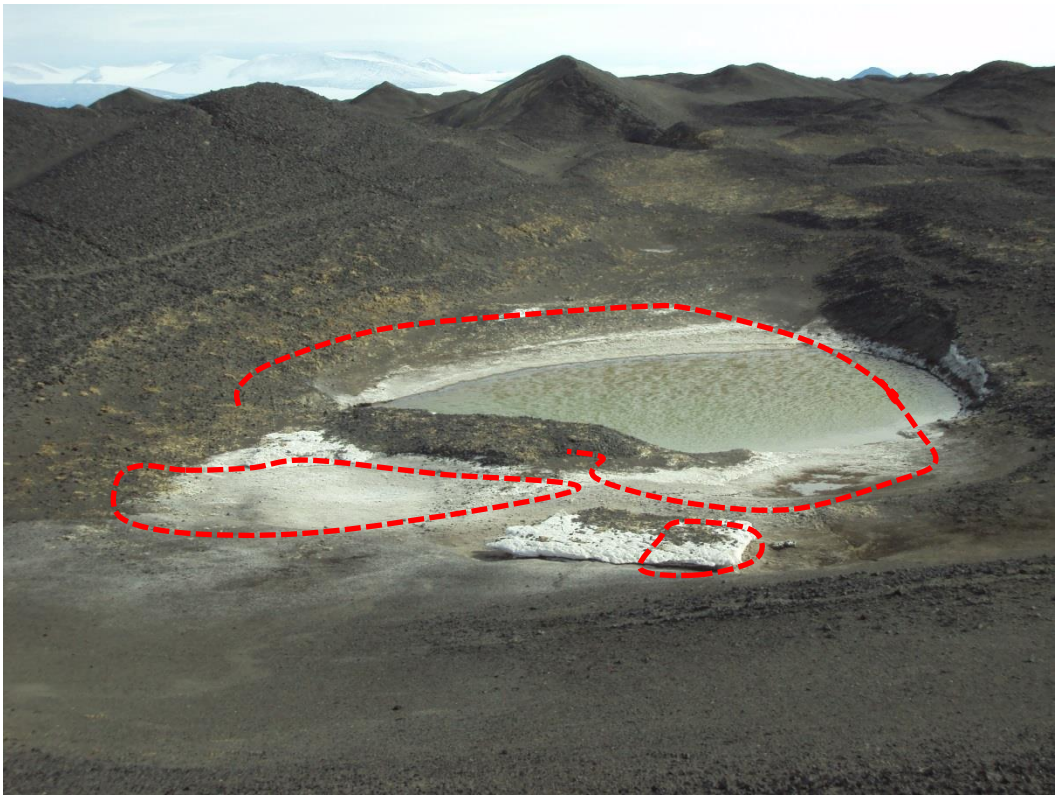
Fig. 3.4 Orange Pond in 2013

a)

b)

Fig. 3.5 P70 pond in a) 2011 and b) 2013. There are no clear markers visible in the pictures to gauge the increase in pond size between these photographs. However, the disappearance of the old shorelines in the 2011 photo, and the size of the pond relative to the people gives some idea of the expansion. Note also the foam present at the edge of P70 in 2011. 2011 image courtesy of Scott Base staff.

a)



b)

Fig. 3.6 Salt Pond in a) 2011 and b) 2013. The dashed lines show some of the area in 2011 that became submerged in 2013.

Fig. 3.7 Skua Pond in 2013, image courtesy of Claudineia Lizieri

Fig. 3.8 Sampling of foam being blown from Casten Pond, some foam fragments visible on the ground. Image courtesy of Jenny Webster-Brown

3.3 Results

3.3.1 Pond structure and morphology

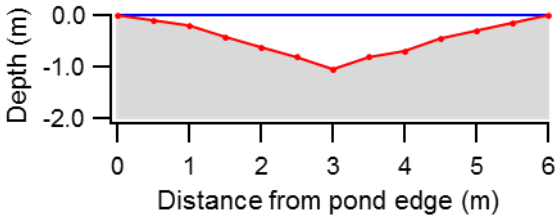
The study ponds ranged in size from 8 × 8 m to 30 × 15 m (Table 3.1). Between samplings in 2011 and 2013, the maximum dimension of Skua and Orange Ponds remained constant, P70 and Salt ponds approximately doubled in size, whereas Fogghorne pond decreased in length by 2 m. The drop in pond level at Fogghorne pond exposed microbial mat that extended beyond the pond edge in 2013 (Fig. 3.3b). Ponds were approximately conical in shape (Fig. 3.9a), and while the pond floor generally continued the subaerial ground relief, some salinity stratified ponds had a small central sump where the slope steepened, as shown on the Huey pond profile (Fig. 3.9b).

Lateral soil profiles showed the depth of ice cemented ground was on average 45 cm below the soil or sediment surface, ranging from 36-53 cm at the study ponds, and all other sites tested in the area (Fig. 3.9). This included a transect from 1 m into each of P70 and Fogghorne ponds to the edge of their catchments (ice cement at depth of 36 – 47 cm, n=9 at P70, 40 – 44 cm, n = 6 at Fogghorne), the centre of a 2.5 m diameter pond (50 cm), and the centre of three evaporated ponds (43-53 cm, n=3).

Surface soils were visibly moist in the margin 1-2.5 m around the ponds' edges, with the more laterally extensive moist zones occurring in the less steep areas of the catchment. Beyond this margin, moist soil was present only beneath the surface. At P70 Pond (Fig. 2c), for example, the depth to moist soil increased with distance from the pond; from 0.2-4.5 cm below the surface near the pond, to 25 cm below the soil surface near the catchment edge. Water-saturated soil sat directly on top of the ice-cemented ground at the pond edge, and extended laterally 2-4 meters beyond the edge of the pond, consistent with a water table continuous with the pond water. At P70's southern margin, saturated soil extended approximately 2.6 m beyond the pond edge, and 0.4 m above the pond level (Fig. 3.3.1c). Pond structure models were constructed based on aspects of all measured ponds (Fig. 3.9).

The volumes of the pond reservoirs in 2013 are presented in Table 3.1. The largest pond was Salt, which had 120 m^3 of water and 230 m^3 of sediment, while the smallest, Fogghorne, had 13 m^3 of water and 84 m^3 of sediment. The volume of saturated soil was 12-41 % of the volume of sediment, highest in Fogghorne pond which was long and narrow, with a large perimeter compared to the pond size.

a)



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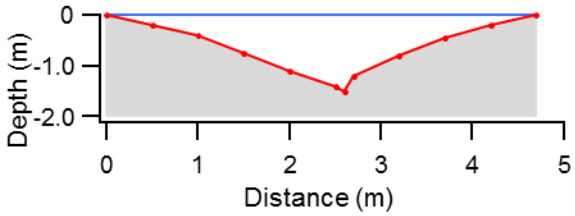

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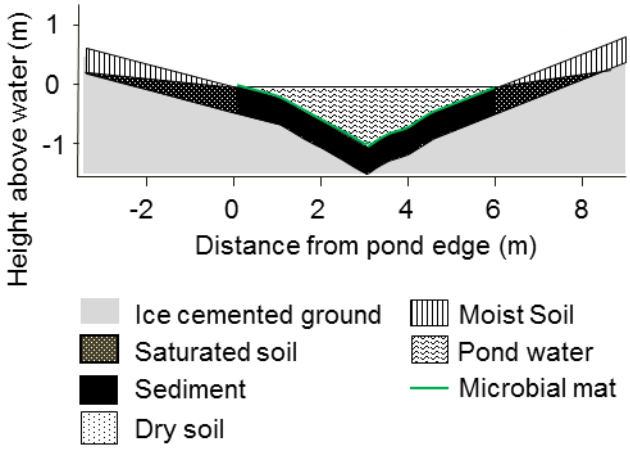


d)

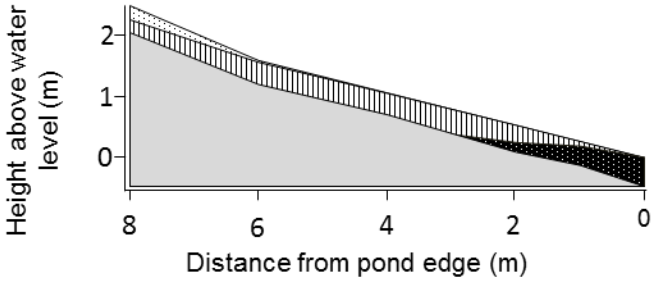


Fig. 3.9 Pond bathymetry and soil profiles of selected study ponds.

a) Bathymetry of Son of Skua pond
b) Bathymetry of Huey pond, an example of a small stratified pond
c) P70 pond soil profile, on a transect that was measured and sampled to the South of the pond.
d) Example of a typical pond structure, using bathymetry data from Son of Skua pond, and a soil profile based on data collected from P70 and Fogghorne ponds.

Table 3.1. Physical characteristics of pond reservoirs, and reservoir sizes in 2013, with 2011 data in italics where available. * denotes a measurement taken within the pond catchment, but not directly adjacent to a pond.

	P70	**Fogghorne**	**Salt**	**Skua**	**Orange**
Length (m)	16 *8*	14 *15*	30 *12*	20 *20*	10 *10*
Breadth (m)	20 *8*	5 *6*	15 *10*	8 *9*	10 *8*
Temperature (°C)	0.7 *0.5*	0.7 *0.7*	1.0 *0.5*	1.0 *1.0*	1.0 *0.9*
Depth estimate (m)	0.7 *0.5*	0.7 *0.7*	1 *0.6*	1.2 *1.2*	1 *0.9*
Permafrost depth (m)	0.47	0.45	0.43*	0.42*	0.45*
Mat cover (%)	100 *100*	100 *100*	100 *100*	100 *100*	100 *100*
Calculations of reservoir volume					
Pond water (m^3)	58.6 *8.4*	12.8 *16.5*	117.8 *15.7*	50.3 *47.1*	26.2 *18.8*
Microbial mat (m^3)	0.036 *0.114*	0.168 *0.205*	1.01 *0.215*	0.414 *0.421*	0.201 *0.159*
Sediment (m^3)	135 *25.6*	37.9 *46.4*	228 *48.2*	93.1 *94.5*	45.2 *35.7*
Saturated soil (m^3)	23.8 *14.0*	15.5 *16.4*	28.2 *16.9*	19.9 *20.4*	15.9 *15.0*

3.3.2 Pond reservoir chemistry

Water reservoir

In 2011, the ponds varied in conductivity from 1.03 – 51.4 mS/cm, and in pH from 8.7 – 10.05 (Table 3.2). These parameters did not appear correlated. Salt pond had the highest conductivity and a pH of 9.81, while Skua pond had the lowest conductivity and a pH of 9.5. In 2013, the conductivities of all of the ponds had reduced by 5 – 45 % relative to 2011 values. This was most pronounced in P70 and Salt ponds, which had also undergone substantial increases in pond size. Water pH varied from 9.58 – 10.38 in the ponds, a higher range than in 2011, however individual ponds had increased and decreased pH values in 2013, with no consistent pattern observed.

Dissolved oxygen concentrations were fairly similar between ponds ranging from 13.92 – 14.24 mg/L (Table 3.2).

A linear relationship was observed across all ponds, and both years, between conductivity and the concentration of Cl, an ion which normally acts conservatively, with a R^2 value of 0.988. Comparison of the molar concentrations of ions showed Na was the dominant cation in all of the ponds, and Mg was more abundant than Ca. Cl was generally the dominant anion, the exception being Salt Pond which was SO_4 dominated.

Total P concentrations in pond water ranged from 70 (Fogghorne) to 1008 (Salt) µg/L. Total water column P was higher in 2013 than in 2011 for all study ponds but Salt, which had slightly less total P in 2013. The dominant form of dissolved P was generally DOP, which was the most abundant fraction in P70, Salt and Orange ponds in both 2011 and 2013, and in Fogghorne pond in 2013 (Table 3.2). All study ponds had greater concentrations of PP in 2013 than 2011, with the most pronounced increase of 9 to 41 µg/L measured in Fogghorne pond. PP was the second most abundant form of water P in 3 of the 5 ponds. Skua pond had markedly different water column P to the other study ponds, and was dominated by DRP in both sampling years. DRP was more abundant than TIN in four of the study ponds in 2011, the only year TIN was measured. The exception was P70 Pond where the abundances were similar (Table 3.2). The resulting N: P ratios are significantly less than the 16:1 Redfield ratio.

The total P content calculated to be in the pond water reservoir in 2013 ranged from 2 g in Fogghorne pond, to 110 g in Salt pond (Table 3.3). Fogghorne pond had both the lowest P concentrations and the smallest reservoir volumes, whilst Salt had the highest P concentrations and the largest reservoir volumes. P70 pond had 247 µg/L total P, which low relative to its pond size, but a similar total P concentration to those measured in Fogghorne and Orange ponds.

Table 3.2. Pond water chemical characteristics in 2013, 2011 data in italics where available. Data is from one sample unless specified.

	P70	**Fogghorne**	**Salt**	**Skua**	**Orange**
pH	10.38	10.13	9.58	9.65	9.89
	9.79	*8.71*	*9.81*	*9.5*	*10.05*
Dissolved O_2 (mg/L)	13.12	13.35	14.81	12.54	13.23
	14.07	*13.92*	*14.41*	*14.16*	*14.23*
Conductivity (mS/cm)	3.83	1.33	40.8	0.89	1.99
	6.92	*1.62*	*51.4*	*1.03*	*2.10*
TP (µg/L)	247	152	959	533	251
	87	*70*	*1008*	*164*	*89*
DRP (µg/L)	50	37	22	442	97
	7	*49*	*52*	*112*	*17*
DOP (µg/L)	89	74	596	<1	97
	47	*12*	*724*	*17*	*41*
PP (µg/L)	108	41	341	91	57
	33	*9*	*232*	*35*	*31*
TIN (µg/L)	*8*	*8*	*36*	*8*	*8*
Chl a (µg/L)	2.75	0.88	4.45	1.90	2.59
Cl (mg/L)	1010	246	4210	107	452
SO4 (mg/L)	225	78.1	21300	193	89.3
HCO_3 (mg/L)	183	124	255	62.9	129
Na (mg/L)	667	242	12600	159	373
Ca (mg/L)	31.3	9.87	186	10.8	11.3
K (mg/L)	29.35	9.73	261	5.47	17.48
Mg (mg/L)	65.0	7.64	274	7.83	18.35

Microbial mat reservoir

The microbial mats in the ponds were variable in colour and appearance. In 2013, P70 Pond had orange cohesive mats covering all but a 20 cm margin of the pond floor, which were covered by a non-cohesive brown mat. In Fogghorne Pond the mats looked sediment-like, with a grey surface, and had a green underside and some orange vertical structures up to 5 cm tall. In Salt Pond the mats were an olive green colour with some small vertical pinnacle-like structures. Skua Pond had smooth olive green mats with no vertical structures. Orange Pond had cohesive orange mats with some "liftoff" mats, where portions of the mat have broken away from the pond floor. The mats were typically 2 mm thick in all ponds, and the volume of the microbial mat reservoir in each pond is therefore more closely related to pond floor area, ranging from 0.036 in P70 to 1.01 m^3 in Salt Pond (Table 3.1).

The P content of the mat ranged from 1340 mg/kg of the mat dry weight in Skua Pond, to 2090 mg/kg in Fogghorne Pond mats (Table 3.4). The biomass of the mat per m^2 of pond floor varied between locations within the ponds, and the average biomass varied with time, changing two fold between 2011 and 2013 in Fogghorne and Salt ponds (Table 3.3). Skua Pond (2013) had the highest average biomass per m^2 in 2013, at 2.7 kg/m^2. Salt Pond had the lowest with 0.97 kg/m^2 in 2011. Fogghorne, Salt and Skua ponds all had increases in average biomass between 2011 and 2013, while P70 had a reduction in biomass, and Orange pond stayed relatively constant. The total P content calculated to be in the microbial mat reservoir in 2013, ranged from 40 g in Orange pond, to 100 g in Salt pond (Table 3.3). This is a similar range to that which was calculated in the pond water reservoir.

Table 3.3 Calculated values of pond P reservoir content in 2013. Numbers with × are calculated from 2013 reservoir data with 2012 concentration data, and * denotes calculation from 2011 concentration data and 2013 reservoir data. na = not analysed.

	P70	**Fogghorne**	**Salt**	**Skua**	**Orange**
Water reservoir P					
Total P (g)	15	2	110	27	4
DRP (g)	2.9	0.5	2.6	22.2	0.4
DOP (g)	5.2	0.9	70	nd	2.5
PP (g)	6.3	0.5	40	4.6	1.5
Mat reservoir P					
Mat P content (kg)	0.04	0.04	0.1	0.07	0.04
Sediment reservoir P – 2013 data only					
Total P in 45 cm (kg)	430	140	760 ×	150 ×	150
Reactive P total (kg)	13	6.5	29 ×	26 ×	6.3
Apatite P total (kg)	370	130	570 ×	150 ×	130
Total P in 5 cm (kg)	48	16	84 ×	17 ×	17
Porewater DRP in top 5 cm (kg)	0.11	0.23	na	na	0.02
Reactive P in top 5 cm (kg)	1.4	0.72	3.3 ×	2.8 ×	0.70
Apatite P in top 5 cm (kg)	41	14	64 ×	17 ×	14
Saturated soil reservoir P					
Total P (kg)	130	73	150*	na	79
Reactive P (kg)	2.5	1.7	2.4*	na	1.5
Apatite P (kg)	110	59	120*	na	66

Table 3.4. Pond microbial and substrate chemical characteristics in 2013. Data from 2011 is presented in italics where available. Data is from a single sample unless an n value is specified, in which case an average is given. Values with × are from samples collected in 2012. na = not analysed.

	P70	**Fogghorne**	**Salt**	**Skua**	**Orange**
Microbial mat					
Mat biomass (kg/m^2)	1.01 (n=3)	1.99 (n=3)	2.01 (n=3)	2.70 (n=3)	2.38 (n=3)
	2.50 (n=5)	*1.19 (n=5)*	*0.97 (n=5)*	*1.89 (n=5)*	*2.45 (n=5)*
Mat P (mg/kg)	1230 (n=3)	2090 (n=3)	1350 (n=3)	1340 (n=3)	1860 (n=3)
Sediment – top 5 cm					
Total P (mg/kg)	1590 (n=2)	1830	1670×	815 ×	1700 (n=2)
Pore water DRP (mg/L)	0.25 (n=5)	0.29 (n=5)	na	na	0.035 (n=5)
Reactive P (mg/kg)	45.9 (n=5)	85.2 (n=5)	64.5 ×	137 ×	70.0 (n=5)
Apatite P (mg/kg)	1360 (n=5)	1720 (n=5)	1260 ×	828 ×	1390 (n=5)
Soil					
Total P	2808	2359	*2614*	na	2478
Soluble P (mg/kg)	52.7 (n=4)	56.2	*43.0*	na	47.7
Apatite P (mg/kg)	2230 (n=4)	1920	*2200*	na	2080

Sediment reservoir

A sediment sample from Fogghorne pond was comprised of albite (75 %), quartz (10 %) and diopside (15 %). Sediments contained 815 – 1830 mg/kg of total P (Table 3.4). The values calculated for the reservoir include a 45 cm value, which encompasses the entire reservoir, and a 5 cm value, which is in closer contact to the pond for potential P exchange. Depth of the sediment reservoir is a key factor in calculating reservoir size, as each cm represents a large volume of sediment. The total P content calculated to be in the sediment reservoir in 2013, ranged from 140 kg in Fogghorne pond, to 760 kg in Salt pond (Table 3.3). This makes the sediment the principle P reservoir in the ponds, containing 3-4 orders of magnitude more P than the water and mat reservoirs. The one exception of Skua pond, had approximately half the total P concentration measured in sediments from the other ponds. Sediment P was comprised

predominantly of apatite P (86 to 97 %) in all 5 ponds studied (Table 3.4). Reactive P fractions comprise only 3-5 % of the total P in four of the study ponds, and 14 % in Skua pond.

Sediment cores from P70, Orange and Fogghorne ponds contained on average 1.4 to 1.8 g/kg of Psenner extractable P in the top 5 cm (Fig. 3.10 a-c). The lowest total Psenner extractable P, and lowest concentrations of each fraction were measured in P70 pond, and the highest in Fogghorne Pond. Exchangeable P made up less than 1 % of the total P, and was the most variable fraction, ranging from 0.2 – 5 mg/kg in P70 and Orange ponds, and from 0.07 – 10 mg/kg in Fogghorne pond. Exchangeable P behaved fairly consistently in the three ponds, present at the higher concentrations in the top layers of sediment and mat material, and decreasing an order of magnitude or more over the 5 to 12 cm depths of the cores. Both Fogghorne and Orange ponds showed a deeper zone of high exchangeable P at 5 – 6 cm depth in the core. This was not seen in the core from P70 pond, which was only 5 cm long due to rocky substrate.

P bound to reducible oxide phases (RO-P) was present at a higher concentration than exchangeable P, except for the top 8 cm of the Fogghorne Pond core. RO-P was present at 4 – 15 mg/kg in the cores at P70 and Orange ponds, with the highest concentration at the top of the cores, and generally decreasing with depth. At Fogghorne pond RO-P ranged from 2-21 mg/kg, the greatest concentration was measured at 10 cm depth, with no clear relationship shown between concentration and depth. MO-P made up 3-4 % of the total P in the cores, and its concentrations were much more stable with depth. There was a slight decrease 5 cm below the surface in Fogghorne and Orange ponds. The depth over which the greatest change in reactive P fractions occurred in each core, was between 1.5 and 2.5 cm in P70 pond, below 5 cm in Orange pond, and below 6 cm in Fogghorne pond, where the reactive P decreased in concentration. Apatite P varied between 1.2 g/kg and 1.8 g/kg in the cores, and did not show a consistent change with depth (Table 3.4 and Fig. 3.10).

Sediment pore waters were not able to be extracted from every sample in the cores, however for those where it was obtained, there was a pattern of increased DRP relative to pond water in the pore waters (Table 3.4).

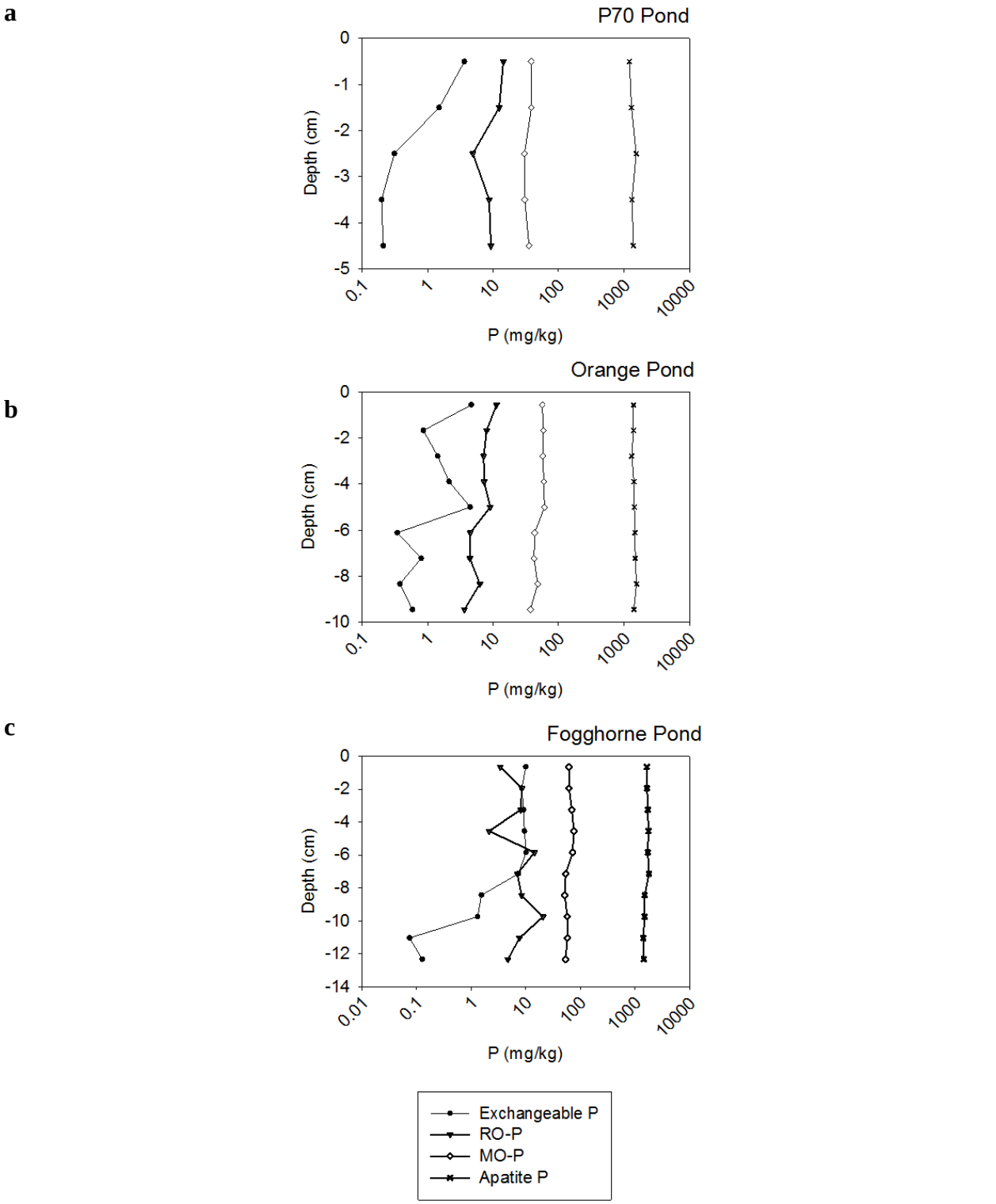


Fig. 3.10 Sediment Psenner fractionation data for cores collected from a) P70, b) Orange and c) Fogghorne ponds. No cores were taken from Skua or Salt ponds.

Soil reservoir

The soils at Bratina Island were visibly uniform, grey-brown in colour, and appeared dry and loose unless directly adjacent to the ponds. One sample from Fogghorne pond was comprised of albite (75 %), quartz (15 %) and diopside (10 %), a similar mineral composition to the sediment sample from Fogghorne pond. Many ponds had a rim of soil salts extending 1-3 m from the pond margin, often at the edge of the visibly moist soil that surrounded the ponds. Salt crystals in these soils included halite, sodium sulfate (appeared to be mirabilite), and unidentified rectangular crystals comprised of mixed K, Na, SO_4 and Cl. No detectable P (i.e., < 1atomic %) was present in any of the analysed salt crystals.

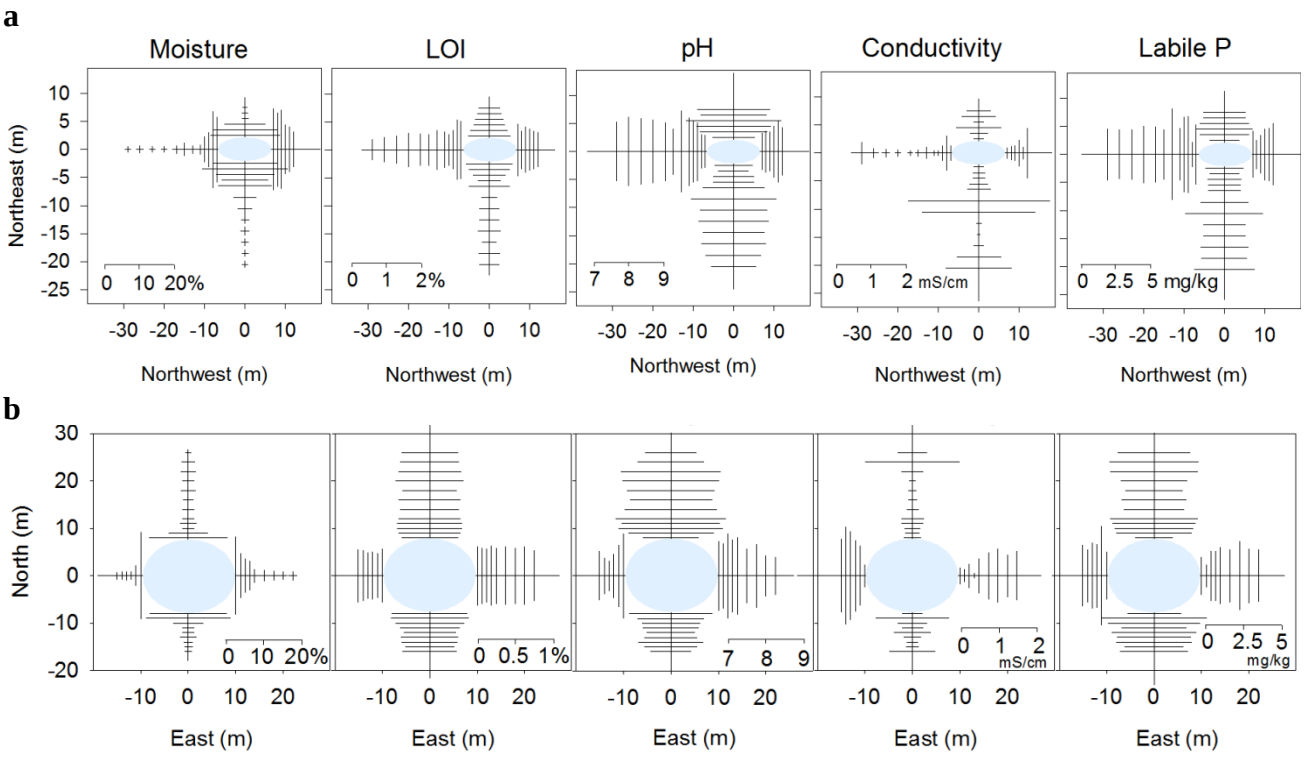


Fig. 3.11 Soil characteristics of two study ponds

a) Fogghorne pond soil parameters are shown. The bar length relates to the magnitude (as shown on each scale) of each variable, and the bar position relates to the location the soil sample was taken relative to the pond.

b) P70 pond soil parameters. The bar length relates to the magnitude (as shown on each scale) of each variable, and the bar position relates to the location the soil sample was taken relative to the pond.

The soil transects at P70 and Fogghorne Ponds showed that soil moisture and mass loss on ignition (LOI) decreased with distance from the ponds, with both parameters stabilizing about 8 m from the pond edge (Fig. 3.11). Elevation above the pond water level is likely to have a greater influence on soil moisture than distance from the pond edge, but this could not be measured accurately. Catchment soils had pH values that ranged up to 10. At Fogghorne Pond, soil pH increased with distance from the pond where the soil was moist, with lowest values (<8.5) right at the pond edge. This pattern was not present at P70 pond, and soils at the pond edge ranged from pH 8.5 – 9.25. Labile P concentrations varied more than 3 fold in the Fogghorne Pond catchment. Low labile P concentrations were measured immediately adjacent to the ponds, and at Fogghorne pond the samples 1-2 m from the pond edge also had relatively low labile P, but otherwise did not show a consistent pattern with distance from the pond in each transect. The south western transect at Fogghorne pond had the highest labile P concentrations, as well as the lowest conductivity samples. Soil conductivity on the other transects varied more than tenfold, with the highest conductivities coming from samples taken in the ring of soil salts surrounding the ponds.

Hedley extractable total P concentrations ranged from 2280 (P70 Pond) to 2630 mg/kg (Salt Pond) (Table 3.3). The dominant form of P in all soils was apatite P, which made up 97 % (Fogghorne Pond) to 98 % (P70 Pond) of the Hedley extractable total P (Fig. 3.12). The reactive P was dominated by metal oxide bound and organic P (MO-P), which comprised 1.3-1.5 % of the Hedley extractable total P at the ponds. Soluble P was more abundant than labile P at Fogghorne, Salt and Orange ponds, where concentrations ranged from 8.6-16.0 mg/kg, and at P70 soluble P was the smallest fraction with 9.4 mg/kg.

The saturated soil reservoir of the study ponds contained 73 kg (Fogghorne) – 150 kg (Salt) kg of total P (Table 3.3). This makes saturated soil the second largest reservoir of P in the ponds, with several orders of magnitude more P than the pond water and mat.

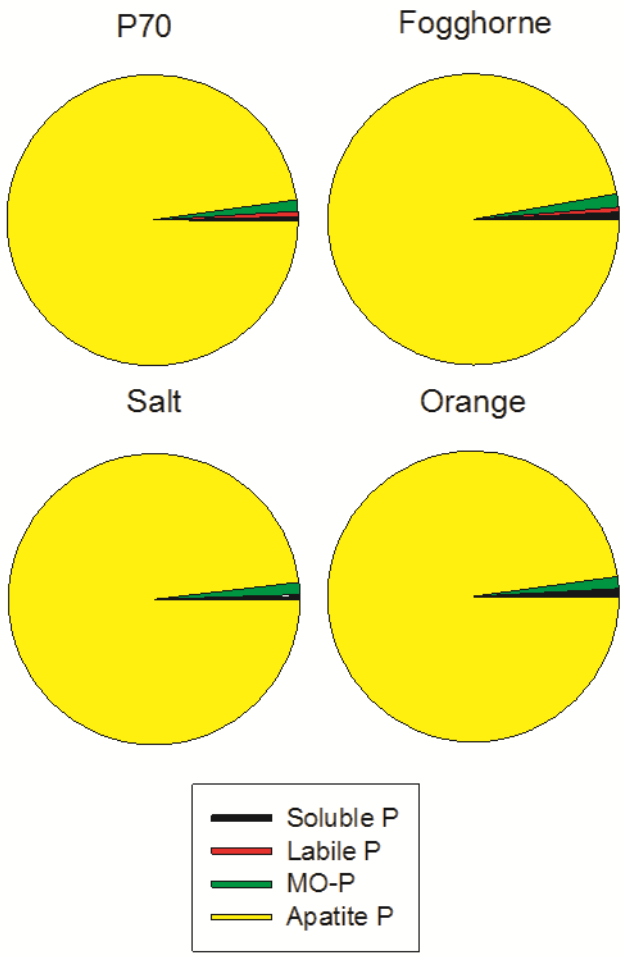


Fig. 3.12 Hedley fractionation data from soils in close proximity to the four sample ponds. The data for Salt, Fogghorne and Orange ponds are from a single sample from 2011, while the P70 data is the average of 4 samples from 2013.

Pond sediments contained only 70 – 80 % of the total P in surrounding soils, except for Fogghorne pond where sediments contained 93 % of the soil P concentration (Table 3.4). Surface sediment at Fogghorne and P70 ponds contained less exchangeable P than adjacent soils (Fig. 3.13), with consistently less RO-P in the sediments, particularly at Fogghorne pond. Interestingly, the two ponds show almost opposite patterns in the MO-P fractions with distance from the pond. Fogghorne pond had a relatively high MO-P fraction in the sediments, which decreased with distance from the pond. Whereas in P70 pond, the sediments show the lowest concentration of this fraction, and the highest concentration is seen in the soil sample furthest from the pond. There was a dramatic difference between the exchangeable P concentrations in

the sediments at P70, and the soils which had much higher concentrations. Exchangeable P at Fogghorne had varying concentrations with distance. The lowest concentration measured was in soil 3 m from the pond, rather than in sediment. The apatite P concentration was generally lower in sediments than in soils at both ponds, except for the soil sample 3 m from Fogghorne pond, which also had the low exchangeable P concentration.

There was a general trend seen between the four study ponds where soil and sediment total P were measured, which showed lower total P concentrations in sediments were correlated with lower total P concentrations in soils (Fig. 3.14).

Soil samples visibly affected by skua guano had labile P concentrations in ranges similar to the soils from transects around P70 and Fogghorne Ponds. Of the four samples that were visibly effected by guano, three samples had higher labile P concentrations than the control samples taken nearby without visible guano (Skua effected/control = 3.48/1.97 mg/kg, 15.00/1.33 mg/kg, 1.47/0.89 mg/kg). However the fourth sample had less labile P than the control, with 2.31 mg/kg in the effected soil, and 14.05 mg/kg in the control.

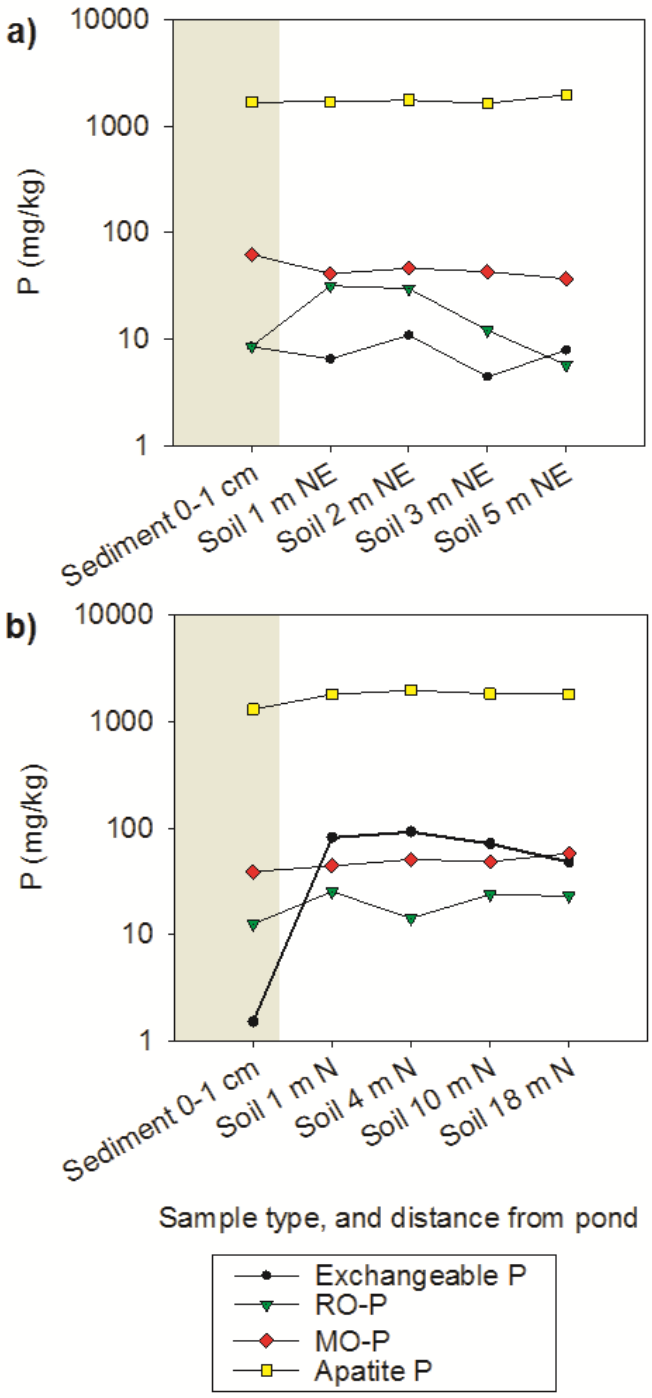


Fig. 3.13 Soil Psenner P fractionation data for transects

a) PSenner fractionation data of 4 samples of soil from a transect to the north east of Fogghorne pond, and the data from sediment beneath the algal mat from 0 – 1 cm depth in the pond, depicted by light grey shading. This pond had recently dropped in level.

b) Psenner fractionation data of 4 samples of soil from the northern transect from P70 pond, and the data from sediment beneath algal mat at 1 cm depth in the pond (light grey shading). The pond level had recently increased.

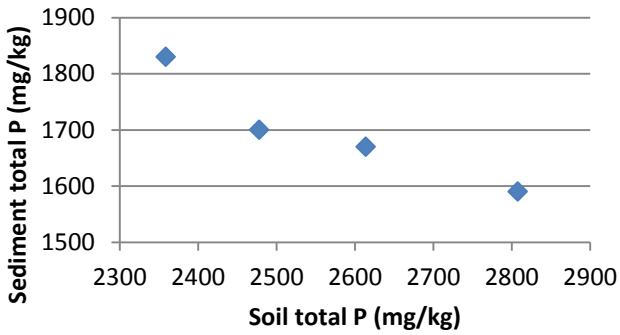


Fig. 3.14 A plot of the total P concentration in the soil reservoir of ponds versus the total P content in the sediment reservoir.

3.3.3 Atmospheric sources – P chemistry

Atmospheric sources of P include snow, aerosols deposited with the snow, and other material transported by wind. Unfortunately snow was not present during sampling times, and so a sample from the nearby Ross Island at Cape Royds has been analysed as a proxy. The melted sample contained 5 µg/L DRP, and 0.66 µg/L DOP; much lower concentrations than were measured in the pond water.

The dust collectors collected wind-blown particles, and deposition onto the collectors varied considerably; the two collectors at Orange pond collected 0.01 and 0.05 g of dust, while the collectors at Skua pond collected 0.15g and 77.25 g. At both ponds the collector to the South of the pond collected more dust. The collectors with 0.15 g or less of dust, had fine particles, with labile P concentrations of 111 – 183 mg/kg. However, the sample from the southern side of Skua pond with 77.25 g of material had coarser grains than that seen in the other samples, and visible mat fragments. The labile P concentration in dust from this sample was 9.3 mg/kg. This same sample to the South of Skua Pond collected ca. 150 mL of snow melt, which after the dust was removed by filtration contained 0.68 mg/L DRP. The dust had been in the melted snow sample for an unknown period of time during the collection period of 17 days.

A single sample of foam, which was present on the edge of Casten pond, and from which some was observed being transported from the pond by wind, had 37.5 mg/L total P in the residual liquid. This was mostly in the form of DOP (25.3 mg/L), with 11.8 mg/L of PP and 0.5 mg/L DRP.

3.3.4 Stratified pond water chemistry

Huey pond and P70E ponds were chemically stratified at the time of sampling, with chemoclines present below 80 cm, and 60 cm depth respectively (Fig. 3.15). In Huey pond, the measured parameters were similar in the layer from the pond surface to the start of the chemocline, below which DRP, TP and conductivity increased by more than an order of magnitude with depth (Fig. 3.15a). Water temperature increased from 1.4 to 6.8 ºC, while pH decreased from 9.5 to 7.1 down the water column. DO concentrations initially increased with depth, and exceeded the maximum (22 mg/L) able to be measured by the meter from 90 cm. Below 125 cm depth the DO concentration decreased to 11.8 mg/L at the base of the pond.

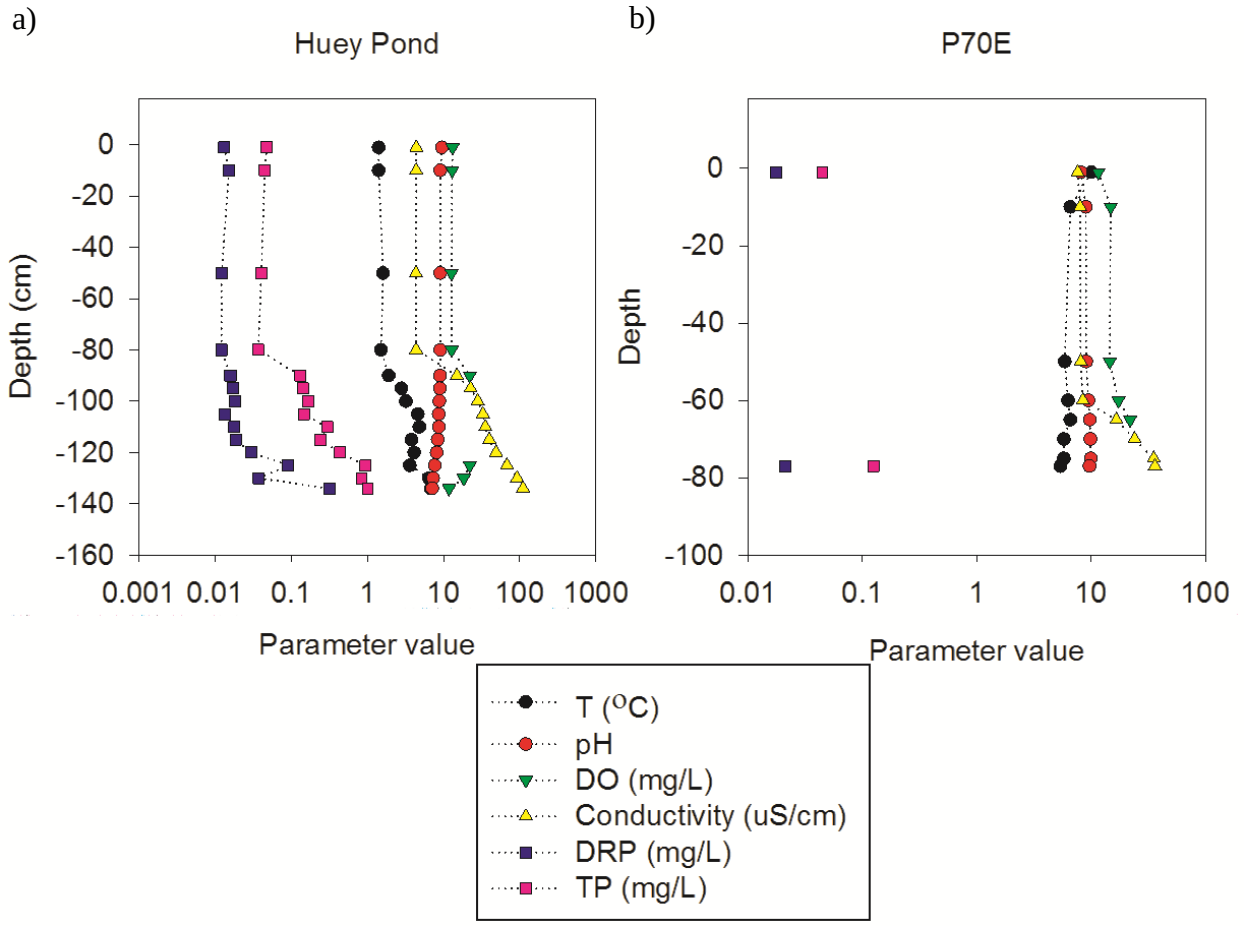


Fig. 3.15 Depth profiles of key parameters in two stratified ponds. The unit for each parameter is displayed on the legend. The DO meter had a maximum reading of 22 mg/L, which was exceeded from 90 to 125 cm depth in Huey pond, and from 65 cm depth in P70E pond.
a) Huey pond b) P70E pond

A correlation was observed between conductivity and TP concentration in the Huey pond water column (R^2 = 0.91, Fig. 3.16). However this was not observed between conductivity and DRP concentration (R^2 = 0.56, Fig. 3.16). The TP concentration in the water column includes DRP, DOP and PP, and in the mixed surface waters of Huey pond, DRP makes up approximately one third of the TP concentration. Below the chemocline, only 4 – 12 % of TP is in the form of DRP with the exception of the basal sample, which has 31 % DRP, similar to the surface waters.

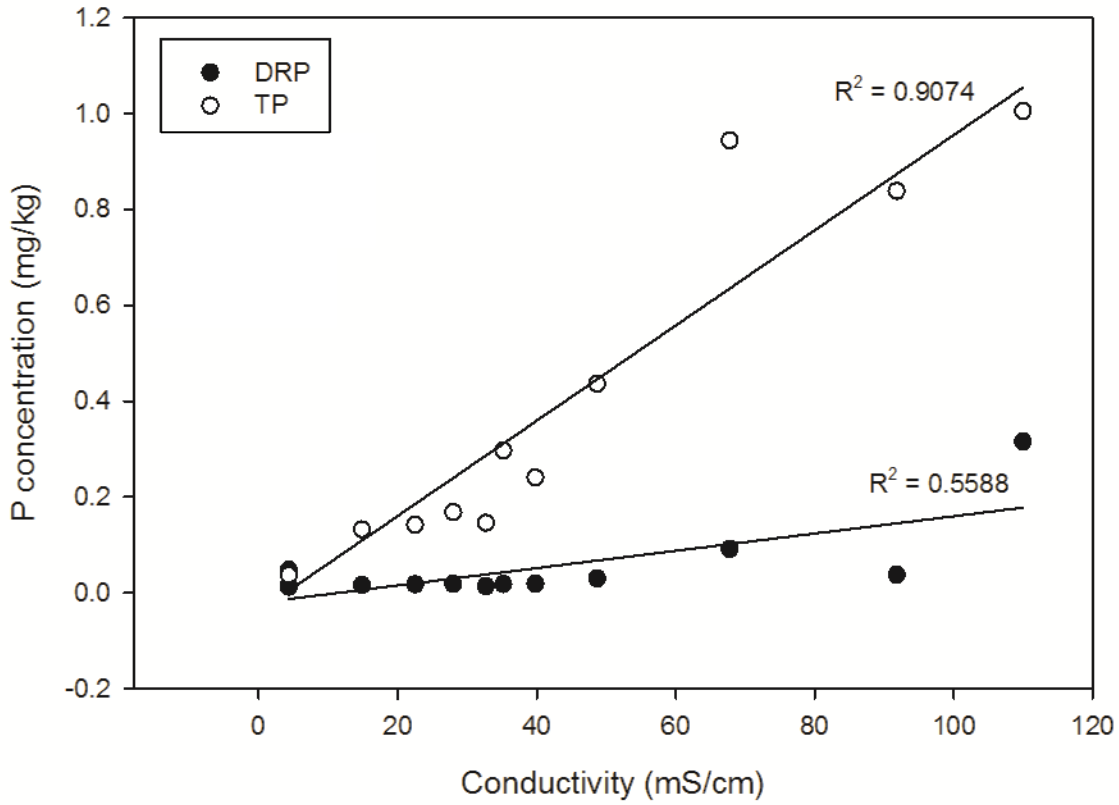


Fig. 3.16 The relationship between conductivity and P concentration in Huey pond in January 2013.

In P70E pond, the stratification was slightly different, and as well as the chemocline below 60 cm depth, the water at 1 cm depth had different chemistry to the underlying pond water (Fig. 3.15b). Below the chemocline, conductivity and DO concentrations increased at the base of the pond, with DO remaining above 22 mg/L below 65 cm depth. Temperature and pH showed inverted patterns to those seen in Huey pond. Temperature decreased from 10.1 to 5.4 ºC down the water column, while pH increased from 8.16 to 9.71. Basal pond water had greater P concentrations than surface water (0.021 mg/L DRP and 0.12 mg/L TP in basal water, 0.018

mg/L DRP, and 0.045 mg/L TP in surface water). There appeared to be a surface layer in P70E pond that was not well mixed with the underlying water column. Between 1 cm and 10 cm depth, pH increased from 8.16 to 9.01, and temperature decreased from 10.1 to 6.6 ºC. The changes in these two parameters are greater than those measured below the chemocline at the base of the pond.

3.4 Discussion

3.4.1 P distribution in pond reservoirs

The major P reservoir in all ponds was the sediment, which contained 65-83 % of the total pond P (Table 3.4, Fig 3.17). Around the margin of the ponds the saturated soil contained a further 16-35 % of pond P, while the microbial mat and pond water column reservoirs, contained much less than 1 % of pond P. The microbial mat and the water column reservoirs had similar total P content in each pond.

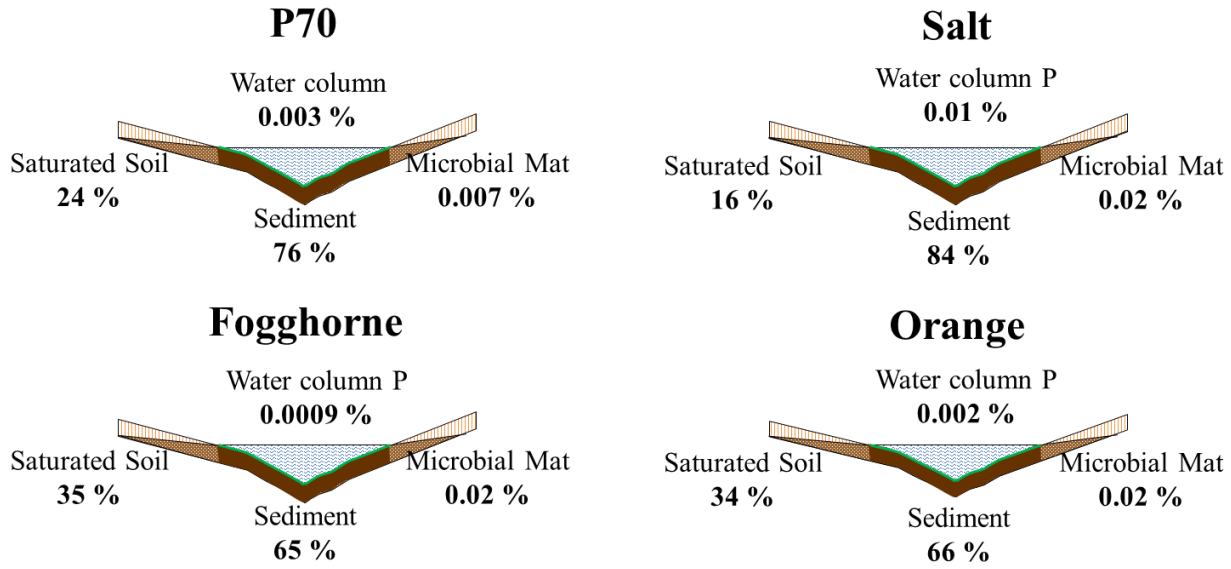


Fig. 3.17 A summary of P distribution between the pond water, microbial mat, sediment and saturated soil reservoirs. Soil data for Skua pond was not collected, so the % P distribution has not been shown.

The absolute and relative size of each reservoir is constrained by the physical pond environment. This is intuitive for the abiotic reservoir volumes, where a larger pond will have larger reservoir volumes. Pond shape is also an important factor, where oval ponds such as Fogghorne have a greater perimeter relative to circular ponds, hence a relatively larger saturated soil reservoir. For

sediments and soils, where P concentrations are in the order of grams per kilogram, a greater reservoir volume will again increase the P content of these reservoirs. The size of each pond is principally determined by input of snow melt in these closed basin systems, and may also have some input from melting basal ice. Skua Pond however had a trickling inflow from a neighbouring pond in 2013, and has previously been documented to have both inflow and outflow some summers. Inflow and outflow to the pond will facilitate greater exchange of water column P, suspended solids and biomass.

Both soils and sediments had a remarkably consistent active (non-permafrost) layer of approximately 45 cm depth throughout the study area. This constrains the volume of sediment and soil which are capable of interacting with the pond in each catchment. These depths in the study area were greater than the 10-20 cm moraine depth that has previously been reported for soils of the ice cored moraine area of the MIS (Howard-Williams *et al.* 1990), and are the first sediment depths reported beneath ponds in the area.

3.4.2 P speciation and availability

Sediment

Sediments are the major reservoir of P for the 5 study ponds, the vast majority (>75 %) of which is in the acid soluble apatite P fraction. The fractionation of P in pond sediments was very consistent across ponds, with increasing concentrations of P in the less available P fractions; exchangeable P $<$ RO-P $<$ MO-P $\ll$ apatite P. Pore water P, and P solubility is dependent on solubility of P minerals, namely apatite (Hesse 1973), adsorption reactions, the solubility of phases that adsorb P, and also remineralisation of organic material.

The Psenner type extraction was chosen for this system because the reactive fractions targeted, are what would be expected to become soluble in the ponds under conditions that have been documented to occur in summer. Reactive P fractions make up 3-5 % of the total P in all but Skua pond, where 14 % of total P is in reactive form. The exchangeable, RO-P and MO-P fractions are the reactive fractions of P in the sediments, and may be released by ion exchange, by metal oxide reduction or high pH conditions. It is well documented through reports of H_2S odour, 0 mg/L dissolved oxygen concentrations, and measurement of H_2S and anaerobic processes that anoxic conditions can arise at the base of ponds and lakes, and beneath the mats,

which will facilitate reduction of iron and manganese (hydr)oxides and subsequent RO-P release (Mountfort *et al.* 2003, Wait *et al.* 2006, Webster-Brown *et al.* 2012). Alkaline conditions are common in the meltwater ponds in summer, with all pH values measured in this study being between 8.7 and 10.38. The desorption extraction step used in this study employed a pH of 10 to desorb P from metal oxides; therefore the high pH values reached in the water column of the ponds during summer, and interaction of pond water with the sediment are capable of causing the MO-P fraction to desorb.

The apatite P fraction will include any P in the form of apatite minerals, the major naturally occurring P mineral in the lithosphere, as well as any P associated with calcium carbonates, or inside the structures of metal oxides. This 'Apatite-P' is generally considered less available than the metal oxide and exchangeable forms, however the lower concentration of apatite P in sediments relative to soils suggests this fraction is being made available to the ponds. Chemical weathering of soils and sediments near streams of the Lake Fryxell Basin, Taylor Valley was measured by H_4SiO_4 and HCO_3^- fluxes, and shown to occur at rates comparable to temperate systems (Lyons *et al.* 1997). The reason for this was not certain, but freeze thaw cycles, steep temperature gradients and wetting and drying cycles were proposed as factors which may accelerate the weathering process (Colman & Dethier 1986, Lyons *et al.* 1997). These factors are present in and around the MIS ponds. In the Onyx River, sediments act as a nutrient source for early flows in the river, derived from salts formed as the river dries and freezes, and from rock weathering during winter (Howard-Williams *et al.* 1997). These examples indicate that chemical weathering of minerals occurs at significant rates in Antarctic aquatic systems, and supports the idea that the apatite P in the MIS pond sediments may weather and become available to the pond.

The sediment in the Orange and Fogghorne Ponds cores had increased concentrations of exchangeable P in the top 5 cm of the core (Fig. 3.10 b and c). We propose this is the zone in which recycling of organic material is taking place, and able to act as a source of P to the mat, and the overlying pond water. There have been reported incidents of substantial nutrient release when 'lift off' events have occurred (Hawes *et al.* 1993), and large portions of mat have floated to the top of the pond, allowing the enriched water beneath them to mix with the pond water. This observation is consistent with high nutrient concentrations within the mats and pore waters, and supports the idea presented in Hawes et al (1993) that the mucilaginous matrix of the mats

acts as a barrier, preventing diffusion of nutrients from the sediments to the overlying water. The observed profiles in the sediment cores show high concentrations of DRP and exchangeable P in the top 5 cm, which would work against a diffusion gradient of P from the deeper sediments into the pond water. However, the deeper sediments also have significantly less P than the soils, suggesting that they are still an important contributor of P to ponds, despite this barrier. It is possible that over the lifetime of the pond, and particularly after the microbial mat forms a diffusion barrier, recycling of biological material may slow, or even reverse transport of P from sediments to the pond. This may mean that after mat formation, lift off events and freeze thaw cycles may become key events facilitating P transport from sediments into the waters of mature ponds.

Sediments at all ponds contain less total P than is found in the adjacent soils, suggesting that if ponds form on top of soil, there has been loss of soil bound P to the ponds over time. At Fogghorne pond for example, the sediments contain 1830 mg/kg total P, less than 80 % of the 2360 mg/kg that is found in the surrounding soils. This difference is comprised of both reactive P and apatite P fractions. If we assume that P from sediment is transported to the pond, the difference between the total P in the Fogghorne Pond sediment, and in an equivalent volume of soil was calculated to be 40 kg of P, which is immensely more than the *ca.* 12 g calculated to be present in the water and mats of Fogghorne Pond in 2013. This means that over the ponds lifetime, approximately 40 kg of P may have been released from sediments into the pond water, and subsequently lost from the pond. Sediments are therefore important as a large, and ongoing source of P to the ponds over their lifetimes, and there must be a mechanism for P loss from the ponds over time.

The apparent net loss of P from ponds is supported by several observations in the study area. Explanations include loss of biomass, such as the exposed dry mats at Fogghorne pond in 2013 which can be blown away after pond level decreases. Additionally, after lift-off events occur, the detached mat can be blown to the pond edge where it may dry and be wind transported. Visible mat fragments were collected in the dust collector to the South of Skua pond, confirming aerial transport of biomass. Additionally, the high concentration of P in the foam from Casten Pond (Table 3.4) shows loss via foam is a transport pathway of P both out of, and possibly into the ponds. The lifetimes of ponds at Bratina Island are unknown, however the MIS is a dynamic

environment and large changes in pond catchments and hydrology can occur with shifts in the ice (Howard-Williams *et al.* 1990, Hawes *et al.* 2014). Pond dehydrations will expose microbial mats to desiccation, and enhance biomass and P loss via wind transport.

Soil: Saturated and catchment soils

Saturated soils are the second largest reservoir of P in the ponds, but are likely to be the least available to the pond, requiring transport via diffusion or groundwater flow. The majority of the reservoir's phosphorus is in the form of apatite P, which requires weathering to enter the dissolved phase. The saturated soil phase has more reactive P than is present in the sediments, but fluctuations in pond chemistry that facilitate dissolution of sediment P, will not affect the soil. Soil pH values at Fogghorne and P70 ranged up to 10, however in the saturated soils at the pond edge the pH was < 8.5 at Fogghorne Pond, and between 8.5 and 9.25 at P70 Pond. Therefore some desorption of MO-P may occur in the saturated soil, but biological activity will not occur in the majority of this zone, and so reducing conditions are not likely to develop to release RO-P. The saturated soil is therefore a significant reservoir of P, but it is unlikely to be immediately available to ponds.

The fractionation of P in the catchment soil transects away from Fogghorne and P70 ponds showed markedly different patterns (Fig. 3.13). At P70 Pond, which doubled in size from 2011 to 2013, the soils have concentrations of exchangeable P greater than the RO-P and MO-P fractions. The sediment however, appears to have lost the majority of this exchangeable P, where it is by far the smallest fraction. There also appears to be less RO-P, MO-P and apatite P in the sediments than the soils at P70 pond. At Fogghorne Pond, which had a significant reduction in pond size from 2011 to 2013, a very different pattern is seen, where overall the concentrations between the sediment and the soil are similar. The exception being the RO-P fraction, which is present only at very low concentration in the sediment, consistent with the sulfide smell observed during sampling. This suggests reducing conditions were present in the soils, and any reducible oxides would hence be dissolved. Interestingly, the soil RO-P and MO-P concentrations decrease at a distance 3-5 m from the pond edge, while the exchangeable P concentrations vary seemingly randomly, throughout the transect. The drop in pond level is almost certainly responsible for some of the differences seen in this pattern, with the nearby soils having previously leached P into Fogghorne pond. However it is unlikely that the soils at 5 m from the pond and at the

catchment edge were previously submerged, and so some further consideration is required here. It should be noted that the total P concentration in Fogghorne pond soil was much greater than that in the sediment, and so it is possible another fraction was missed from these Psenner extractions that is important in soil leaching.

Microbial mat

The mat reservoir is an active biological reservoir, and is important as the major biomass of the systems, and also as a source of recyclable P. The P concentrations in the mats varied 2 fold, and were in the same range as the total P concentrations measured in the sediments. Mat P could not be speciated, and includes all phosphorus in the mat, and this will include that in living cells, non-living cells, mucilage and in the sediments that are invariably trapped within mat matrices, and which can have a high affinity for phosphate (Webster-Brown & Webster 2007) and will almost certainly be responsible for some of the RO-P, and MO-P observed in the top layers of the sediment cores, which included the microbial mat (Fig. 3.10).

When ponds freeze in the winter (Wait *et al.* 2009), the microbial mat freezes also. A study on mats in the Onyx River in Victoria Land showed that freeze-thaw cycles can facilitate DRP release of 0.1 µg P/cm^2/cycle from thick benthic mats (Howard-Williams *et al.* 1997, Hawes & Howard-Williams 1998). If a similar process occurs in the MIS ponds this would represent an annual pulse of DRP into the pond water as the pond thaws. The benthos was included in the top 1 cm of each sediment core sampled, which generally had higher pore water and exchangeable P concentrations than were seen in the rest of the core. The sediments were frozen for transport back to New Zealand, and the pore water P may have had enhanced DRP released from thawing the mat. During summer, mats sequester P from the overlying water (Howard-Williams *et al.* 1997), and may also release some P back to the pond water via respiration processes. Heterotrophs beneath the mat can recycle abundant nutrients from organic material, and this is likely to be an important nutrient source to the mat (Hawes *et al.* 1993).

Water

Water column P varied in both concentration and speciation between the ponds. In Salt, Orange and P70 ponds the major form was DOP. High concentrations of DOP are consistent with previous findings from these ponds (Sorrell *et al.* 2013, Hawes *et al.* 2014), and these authors

have argued that the organic P pool may contain a significant proportion of refractory molecules which become concentrated over time. DOP is produced by biological reactions, and may be produced by organisms within a pond. Hawes *et al.* (2014) measured DOP concentrations of 7 – 34 µg/L in snow and ice samples in the Skua Pond catchment, suggesting an external source of DOP. The very high DOP and conductivity in Salt pond support the idea of concentration of these solutes over time. DRP concentrations were typically exceeded DIN concentrations, and the low resultant inorganic N: P ratio confirms previous studies which suggested any nutrient limitation in these systems would likely be caused by nitrogen availability (Howard-Williams *et al.* 1989, Hawes *et al.* 1993, Sorrell *et al.* 2013).

Skua pond chemistry was distinctive. It had high water column DRP, very little water column DOP, low conductivity, high mat P, and low sediment total P relative to the other ponds. The striking hydrological difference of Skua pond is that it is not a closed basin system, and the effect of flow through the system is likely to be responsible for these differences. Flow through the pond is likely to flush any solutes from the pond, causing the low DOP concentration and conductivity that were measured. Flow may also introduce a sediment load to the pond, which may allow settlement of fine sediments, and subsequent entrainment into the mat. The fact that Skua pond is not a closed system may also account for the observed difference in sediment P composition. Skua pond had a lower total P concentration than the other study ponds, together with a higher concentration of reactive P. It is possible that delivery of fine sediments during stream flow results in a greater proportion of fine sediments with high surface areas, to which reactive P may adsorb. If these settle they will contribute to high reactive P in the pond sediments. The high water column DRP could perhaps be a result of desorption of reactive P from suspended sediments delivered during stream flow.

3.4.3 External sources of P

The McMurdo Ice Shelf meltwater ecosystems have additional P reservoirs; including the catchment soils, the resident skua population, snow precipitation, and dust and windblown material. These reservoirs are more difficult to quantify than the main pond reservoirs described above, and interact with the ponds by more transient means. We have called these reservoirs ‘external’ sources of P to the pond, as they typically require an event to enable transport to the pond from the external source reservoir, in order to become available for in pond P processes.

The moist and dry soils of the catchment, which can be an intermittent source via leaching with snow melt and fluctuations in pond level, have high soluble and labile P concentrations that will readily dissolve in snow melt. The snowmelt collected in the dust trap to the South of Skua pond contained 0.68 mg/L of DRP, 50 % higher than the Skua pond water concentration in 2013, supporting the idea that snowmelt dissolves soluble P and may transport it to ponds.

The snow collected from Ross Island had 5 µg/L DRP, and 6 µg/L TP. Results in Hawes et al (2013) who sampled snow in the catchment of Skua pond however, reported DRP and DOP concentrations much higher than this, 23.5-28.7 µg/L DRP in fresh and old snow, and 7-8 µg/L DOP. These snow concentrations are higher than the DRP measured in P70 and Orange ponds. Snow accumulation data at Bratina Island has not been published, for which snowfall and transport of snow by wind, and ablation of snow will be important factors. If the values reported in Hawes *et al.* (2014) are representative of normal snow in the area then snow may be a significant source of P to ponds.

The soil transect data shows decreased soil pH in the areas of highest soil moisture at Fogghorne Pond, and the north transect at P70. This pattern was also observed in upland ponds of the MDV (Moorhead *et al.* 2003). Labile P was typically found at low concentrations in the samples taken right at the pond edges. Additionally at Fogghorne pond, samples taken 1 m or more from the pond edge also had low labile P. These samples were taken from soils recently exposed by the drop in pond level, and confirm the ability of soils to act as P sources with changing pond levels. The LOI shows that at Fogghorne pond there is increased organic matter in the soils nearer the pond edge. The dried mats exposed by the decrease in pond level will be responsible for the high LOI up to 2 m from the pond edge, but a definite decrease over distance is seen at Fogghorne that is not present at P70. MDV ponds act as sources of organic matter to their catchments, and this appears to happen at Fogghorne pond. This effect may have been exaggerated by the decreasing pond level at Fogghorne. The increasing pond level at P70 over the study period may have submerged the zone where substantial change in LOI occurs.

Windblown dust contained the highest concentrations of labile P that were measured in any of the 1 hour bicarbonate leaches on soils, and the reason for this may be due to the fine particles which have large surface areas for PO_4 to adhere to. The mass of dust deposited varied from 0.01 g to 77.25 g in the four collectors, with the 77.25 g sample being a clear outlier. This makes it

difficult to try to quantify the amount of dust that might be deposited into a pond, as samples tens of meters apart showed orders of magnitude differences after experiencing the same weather conditions. The collectors to the south of the ponds collected more dust than those to the north, likely a product of the prevailing southerly winds in the area.

Skua guano is another source of P to ponds. During 2013 field work, at least 3 breeding pairs of skua were observed in the area shown in the map, with one pair nesting between Skua Pond and the pond to the west. Guano effected soil, and the adjacent control soil both consistently had higher leachable P concentrations than other soils measured in the area. Study of ornithogenic Antarctic soils has shown high concentrations of total N, C and P, with P occurring in inorganic and organic forms, and even as matrix bound phosphine (Zhu *et al.* 2011, Aislabie *et al.* 2014). Skua guano is likely to have similar effects on MIS soils, however low population denisty means these effects are likely to be localised. Guano entering ponds directly will also be a potential source of P to the pond system.

3.4.4 A model for application to other ponds

The results in this chapter have enabled the construction of a numerical model for P distribution in the principal reservoirs of the key study ponds. The results also provide information on the key transfer mechanisms that are important to P cycling in these meltwater ponds (Fig. 3.18). Dust and skua guano both contain high concentrations of labile P, however their patchy distribution makes it difficult to measure a rate at which they may be supplied to a pond. Snow contains low P concentrations, however over the lifetime of a pond snow may be an important P source. Meltwater and soil leaching was unable to be measured, however the presence of soluble P in soils means this potential P source should not be disregarded. The difference between soils and sediment total P concentrations indicates sediments are a major contributor of P to ponds over time.

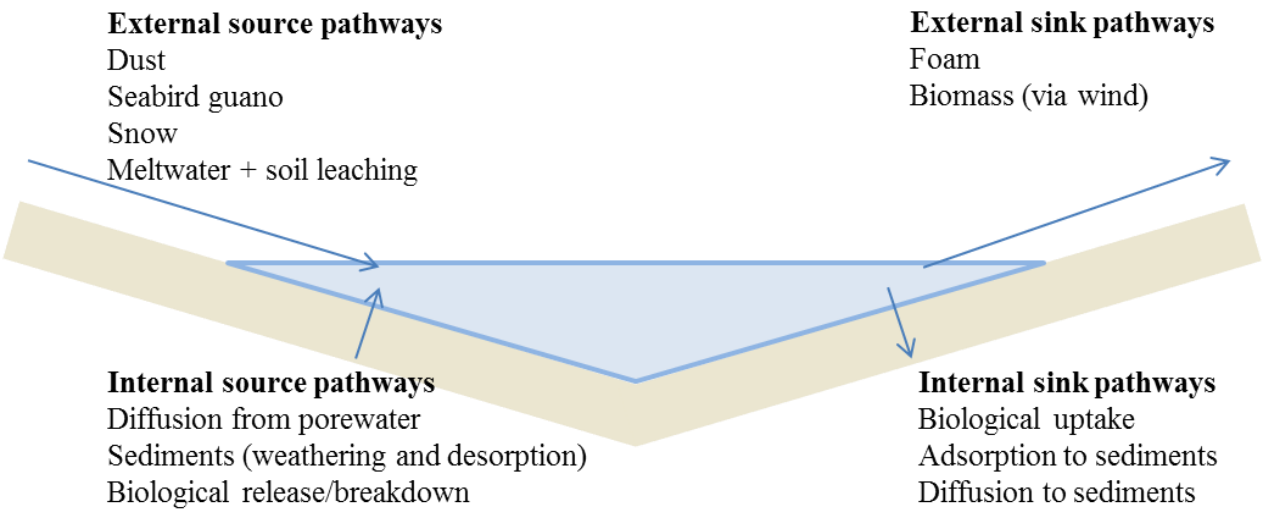


Fig. 3.18 A conceptual model of the P transfer mechanisms that are important to the overall P cycle in MIS meltwater ponds.

The models for P distribution and availability are expected to be applicable to other MIS ponds. The chemical characteristics measured in the ponds (Table 3.2) were typical of sediment lined ponds on the McMurdo Ice Shelf, and consistent with coastal Antarctic ponds in other areas. The conductivity measurements were consistent with data reported by Hawes *et al.* (2013), who performed a study looking at long term variation in McMurdo Ice shelf ponds over 20 years, which included the 5 study ponds in this work. Conductivity and pond size are the only water parameters which are not influenced by biological processes, and changes in these factors, along with water column stratification can give insight into snow and wind activity over the preceding winter and current summer. The conductivity in P70 Pond in 2011, and the 2011 and 2013 conductivities measured in Fogghorne pond were above the 75 percentile reported by Hawes *et al.*, and the 2013 conductivity of Salt pond was below the 25 percentile. The size of P70 and Salt ponds in 2013 was almost double what was measured in 2011, and is likely responsible for the measured decreases in conductivity.

Major ion chemistry was consistent with previously reported data for the area, with Na being the dominant cation in all ponds, and either Cl or SO4 the dominant anion. Nitrate concentrations in 2011 were <2 µg/L, and supported previous work showing a nitrogen limitation in these ponds. Coastal ponds and lakes from other sites in the Ross Sea region, the Syowa Oasis, the Vestfold Hills generally show Na and Cl dominance of major ion chemistry (see review by Torii et al.

1988, Schmidt et al., 1991) , and some of the Ross Island ponds show evidence of N deficiency of planktonic species, similar to the MIS (Vincent & Vincent 1982). This is consistent with a pattern of decreased N concentrations in ponds in coastal, relative to inland areas in the Ross Sea region (Vincent & Howard-Williams 1994). Local differences in geology will be important in determining the P in sediments and soils that are potentially available to ponds, however similar pond chemistries, and perhaps similar temperature regimes at low elevations near the coast may mean that similar processes govern P dynamics in these coastal systems.

A factor that can influence solute distribution in the water column is a residual chemical gradient left from thawing of a freeze-stratified pond, which is common in McMurdo Ice Shelf ponds (Wait *et al.* 2006). This occurs due to cryo-concentration of solutes at the base of the pond, caused by brine exclusion from ice as a freezing front descends from the pond surface (Wait *et al.* 2009). This solute distribution can persist after melting of the pond if the water column is not mixed. None of the study ponds were stratified in 2013, though Orange, Salt and P70 ponds have been stratified previously (Wait *et al.* 2006, Wait *et al.* 2009). Stratification was not measured in 2011 due to restricted sampling time, however none of the ponds had green-coloured water in the deepest section, a visual characteristic of conductivity stratification (Wait *et al.* 2006).

In Huey pond in 2013, DRP and total P concentrations increased by more than an order of magnitude with depth below the chemocline (Fig. 3.15). The positive correlation between TP concentration and conductivity suggests that the physical processes driving major ion distribution in the pond also drive TP distribution. This was also found by Wait (2011) who showed that ratios of DRP and DOP to chloride were similar throughout the depth of stratified ponds. However, in 2013, DRP concentrations do not show a correlation with conductivity, which reflects the changing composition of TP with depth in the pond. DRP comprises between 28 and 33 % of the total P in the top 80 cm of the pond, and also at 134 cm depth. Between 90 and 130 cm depth 4 – 12 % of total P is in the form of DRP. DO concentrations were highest between 90 and 130 cm, suggesting increased photosynthesis in this zone of the pond. The relatively low DRP concentrations in this zone are likely due to increased DRP uptake supporting the photosynthesis and primary production in this zone. This supports the proposal by Wait (2011) that sub-environments may form in the basal brines of ponds, where nutrient composition is redistributed by biological processes. Additionally, different microbial

communities occur in the distinct physicochemical environments within stratified ponds, which may further drive differences in nutrient composition (Archer *et al.* 2014). Therefore, stratification of ponds can influence both the distribution and speciation of P in the water column.

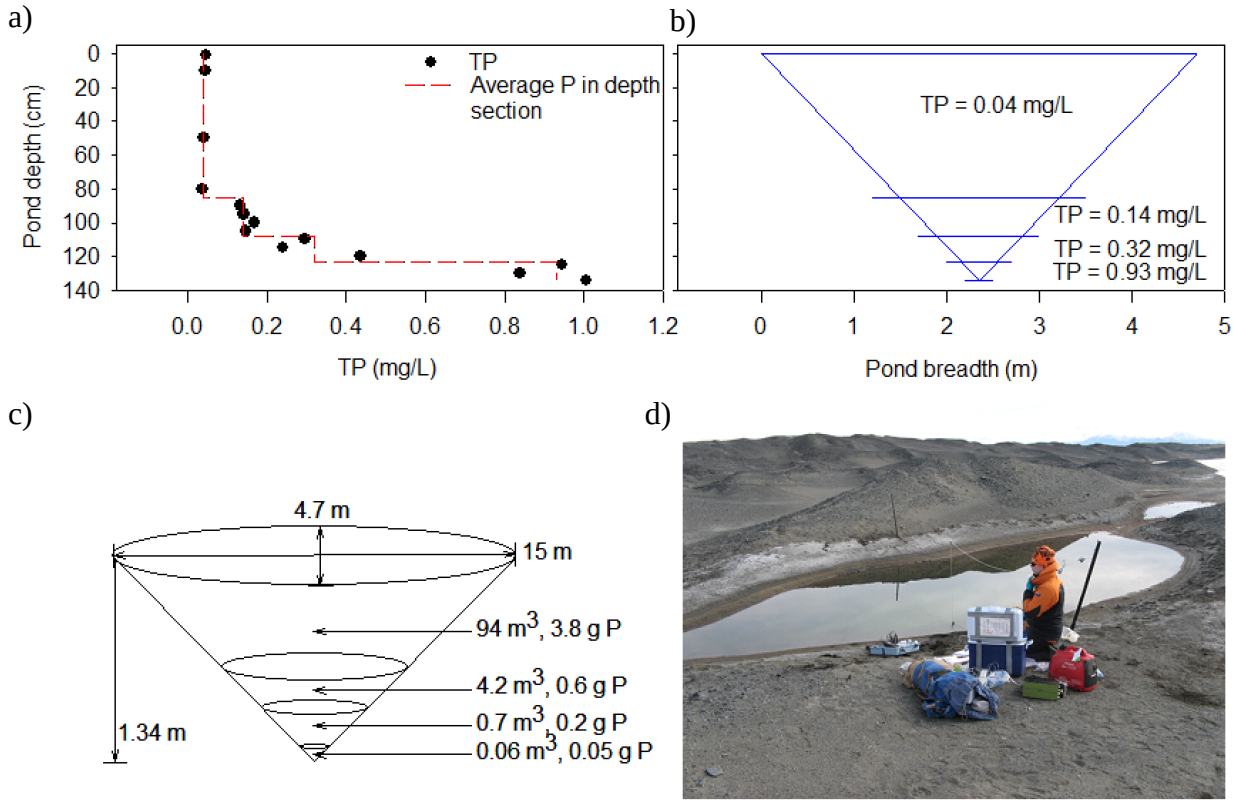


Fig. 3.19 Use of the TP concentration profile in Huey pond to estimate the total P present in the water reservoir at Huey pond

a) The concentration of TP in Huey pond at selected depths (black dots), and the average concentration at selected depth ranges that had similar TP concentrations
b) A cross section of the conical model of Huey pond, showing each depth section, and the TP concentration used to calculate TP for the water reservoir
c) The conical model of Huey pond with the water volume and P content of each section
d) Huey pond

The P content of the water column reservoir at Huey pond was determined in order to establish the influence of stratification on the reservoir. The TP concentration data was used to split the pond in to four zones which had similar concentrations, and the average TP concentration for each zone was used to calculate the P content in that zone (Fig. 3.19). There was 4.6 g of total P present in the water reservoir, the majority of which was in the upper zone of the pond (83 %). Calculation of the water reservoir P from a surface sample only estimates 4.0 g of P in the pond,

an underestimation of 14 %. Although concentrations of TP in the basal brines of stratified ponds are much greater than those in the overlying water, the small volume of the brine means that overall the water column still contains relatively little P. Therefore in stratified ponds, the water column will still only be a minor reservoir of P, and the model developed for non-stratified ponds will likely predict P distribution in stratified ponds also.

3.5 Summary

This chapter characterizes P in ponds on the McMurdo Ice Shelf. The ponds represent coastal systems with low N:P rations, indicating nutrient limitation by N availability.

Key findings:

- Sediment is the largest reservoir of P in McMurdo Ice Shelf ponds, followed by saturated soil, the microbial mat, and then the pond water.
- Sediments are an important source of P over time.
- The soluble and exchangeable P present in the soils seems to be lost rapidly when soils become submerged by rising pond levels.
- Skua guano and dust contain significant labile P and are likely to be important sources of P to ponds.
- Falling pond levels exposes microbial mats, and loss of this biomass as well as foams may remove P from the system.

Chapter 4:
P distribution in inland ponds of the Labyrinth, Upper Wright Valley

Fig. 4.1 An image of the Labyrinth in the Upper Wright Valley, with the Wright Upper Glacier and polar plateau in the background. Some ponds are visible in the troughs of the Labyrinth.

4.1 Introduction

The McMurdo Dry Valleys are the most extensive ice-free area in Antarctica. The meltwater systems contained in these valleys include the iconic large lakes, Antarctica's longest river (the Onyx River), many melt streams, cryoconites, and hundreds of meltwater ponds. The meltwater systems provide habitats for many of the valley's biota, and play key roles in biogeochemical cycling in valley ecosystems.

The Wright Valley is one of the central valleys stretching eastward from the Polar Plateau to the Ross Sea (Fig. 4.2a). Lake Vanda is a central feature of the valley, and has been extensively studied. The area at the western end of the Wright Valley, or the 'Uppper Wright Valley' is called the Labyrinth after the network of troughs carved into the valley floor. Many of the ponds of the Labyrinth at western end of the valley have been studied (Fig. 4.2b), including a chemical characterization of many ponds in the 1980's, and a more recent study of the stratification characteristics in 2004 (Torii *et al.* 1989, Healy *et al.* 2006). This area, for which there is no published data on P concentrations or dynamics, represents an inland system, which is anticipated to contain little P.

Contribution of this research

This chapter addresses research questions 1.3.1 and 1.3.2 for the ponds of the Upper Wright Valley (Chapter 1). The natural abundance and speciation of P in the major reservoirs of meltwater ponds have been identified for five study ponds in the Labyrinth. The reservoirs studied are the sediment, soil, microbial mat and pond water. The biogeochemical cycle concept is then used to interpret the behavior of P in the meltwater ponds.

4.1.1 Chapter Objectives

This chapter aims to characterize P in the ponds of the Upper Wright Valley. The sample site represents an inland system with high N:P ratios, where any nutrient limitation would be caused by P. Characterisation of P in the ponds will involve:

- Establishing the distribution of P in the ecosystem
- Identifying the important reservoirs of P
- Determining the speciation of P in the reservoirs

- Identifying the sources of P to these inland ponds in the Upper Wright Valley

4.2 Site description

The McMurdo Dry Valleys (MDVs) are a series of ice-free valleys west of McMurdo Sound. The major valleys through the Transantarctic Mountains are thought to have been formed by rivers, with subsequent carving by glaciers (Campbell & Claridge 1987). The east-west oriented Wright Valley (77 S 25' S – 162 41' E to 77 33' S – 160 42' E) was carved by a glacier draining the East Antarctic Ice Sheet during the middle Miocene. The head of the valley is confined by a cirque in the Ferrar Dolerite sill which intrudes the Beacon Supergroup sandstones (Fig. 4.1) (Campbell & Claridge 1987). The floor of the cirque contains the Wright Upper Glacier, which is fed by the East Antarctic Ice Sheet. The Olympus Range forms the northern valley walls, and the Asgard Range the south. The mouth of the valley is submerged beneath the Wright Lower Glacier, a lobe of the Wilson Piedmont Glacier. The valley is ice-free for 55 km of its length, making it the longest ice-free valley on the continent (Campbell & Claridge 1987).

Below the Wright Upper Glacier, and extending 7 km east of its terminus, is a geomorphic feature known as the Labyrinth. At 750 – 1000 m a.s.l. (Fig. 4.2) the Labyrinth is a network of channels up to 100 m deep carved into the Ferrar Dolerite of the valley floor (Torii *et al.* 1989, Lewis *et al.* 2006, McLeod *et al.* 2009). There are a number of hypotheses for the origin of this feature, including catastrophic flooding, glacial plucking, salt weathering, and a combination of glacial erosion by wet based ice, subglacial meltwater, and subaerial erosion (Shaw & Healy 1977, Campbell & Claridge 1987). The most recent assessment by Lewis *et al.* (2006) postulated that catastrophic drainage of subglacial lakes, and repeated failure of an ice dam may have led to vast water flows forming the cross cutting channels.

The basement rocks of the Labyrinth consist primarily of dolerite, while bedrock disintegration has resulted in the dolerite rocks throughout the soils in many of the troughs (Campbell & Claridge 1987). These troughs are irregularly shaped, and the walls often consist of steep dolerite columns, with some 'passes' that are less steep between the troughs. There is some soil development associated with the steep walls, and at the base of the troughs there is ground ice within 100 cm of the soil surface (McLeod *et al.* 2009). Cross sections of the troughs are generally asymmetric, and depressions can occur in the centre, or adjacent to a wall.

Ponds within the Labyrinth occur in depressions that have a glacial or snow meltwater source. More than 60 ponds were identified by Torii *et al.* (1989), with some of the same ponds, as well as additional ones being reported by Healy *et al.* (2006). Ponds are typically less than 100 m diameter, ice-covered, and have an alkaline pH (Torii *et al.* 1989). Cation compositions resembled snow and glacial meltwater in the freshwater ponds, and were similar to Lake Bonney and B-1 pond (from Taylor Valley and Victoria Valley respectively) in the saline ponds (Torii *et al.* 1989). The major ion geochemistry of the ponds is typically dominated by Na and Cl, and ion composition is a result of soil salt dissolution and cryoconcentration during freeze/thaw cycles (Healy *et al.* 2006). The ponds have high concentrations of nitrate and sulfate which is thought to be due to atmospheric deposition of stratospheric aerosols. Cyanobacterial mats have been reported in the ponds, however little work on the biology, or biogeochemistry of these meltwater systems has been published to date (Healy *et al.* 2006).

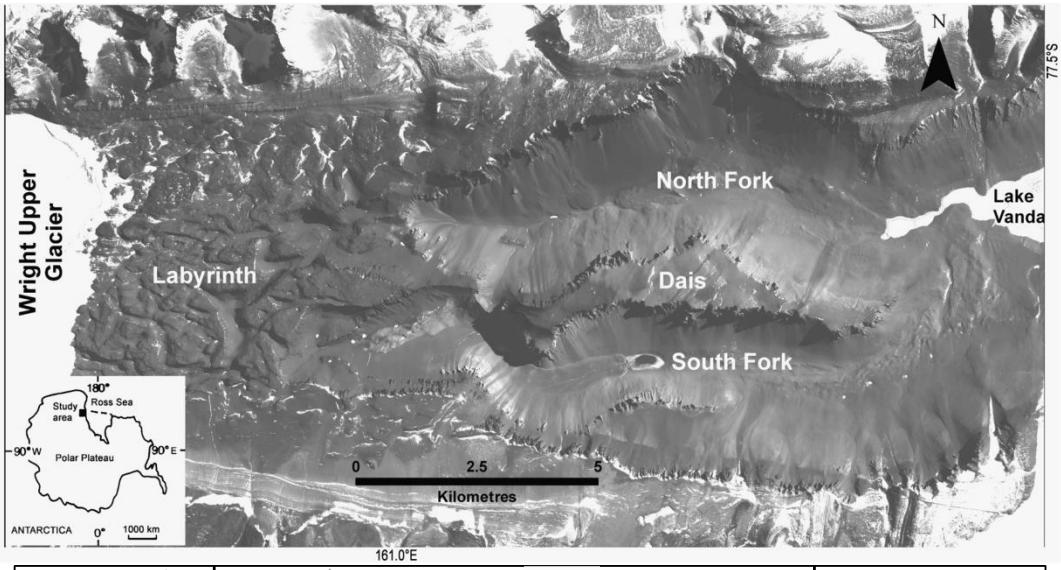
4.2.1 Methods at this study site

For the ponds studied in this chapter, sediment porewater was collected with a MacroRhizon porewater sampler. The MacroRhizon was inserted into the sediment, and a sample was then collected by vacuum into a syringe. This method allowed 20 – 40 mL of porewater to be collected, which was a sufficient volume for both DRP and DOP to be determined. All other sampling and analysis was performed as described in Chapter 2.

4.2.2 Study ponds

Based on the selection criteria outlined in Chapter 2, five ponds were selected to study (Fig. 4.2b). The ponds had a range of conductivities that were representative of the ponds surveyed in the area. Data is presented for an additional two ponds to give a fuller picture of typical pond P characteristics in the area.

a)



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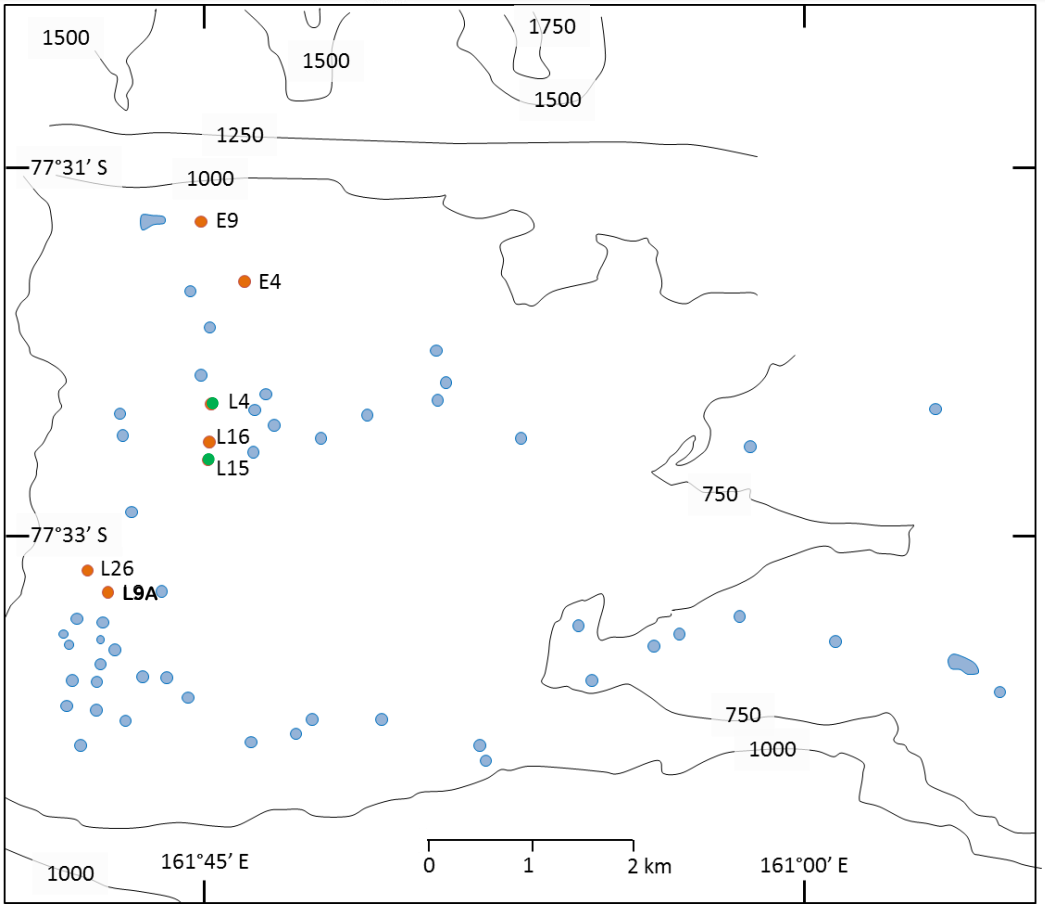


Fig. 4.2 The Upper Wright Valley

c) An image of the Upper Wright Valley taken from McLeod et al (2009).

d) Map of the Labyrinth area of the Upper Wright Valley, modified from Healy (2005). The 5 ponds sampled for this study are depicted by red dots, green dots denote ponds where additional data is presented, and blue dots represent ponds documented by Torii *et al.* (1989) and Healy *et al.* (2005).

E4 Pond

E4 pond is a large, bullet shaped pond that sits in a valley at the base of a large snow bank (Fig. 4.3). The pond surface was frozen, except for an area approximately 15 m^2 at the western end of the pond where sampling was conducted. The cyanobacterial mat was brown and crumbly, and a white salt was present at the base of the pond, both on top of and beneath the microbial mat in some areas.

Fig. 4.3 E4 Pond in January 2012

E9 Pond

E9 pond is a large oval shaped pond which had a connected snow bank, and several other snow banks in the catchment (Fig. 4.4). The pond was entirely covered by thick ice. The microbial mat in the pond was beige, and thin and crumbly in texture. The sample for major ions for this pond was lost due to a faulty tube, during transport to New Zealand. Therefore major ion data for E9 is not presented here.

Fig. 4.4 E9 Pond in January 2012

L9A Pond

L9A pond is a small pond and had a very small snow bank which was the only obvious source of water in the catchment (Fig. 4.5). This pond was mistaken for L9 pond detailed in Healy et al (2006), which lies in the next valley to the south. L9A pond is oval in shape, and had thin ice covering 5 % of the pond surface when it was first sampled, which melted over the remainder of the sampling period. The mat floor was covered by thick orange mats.

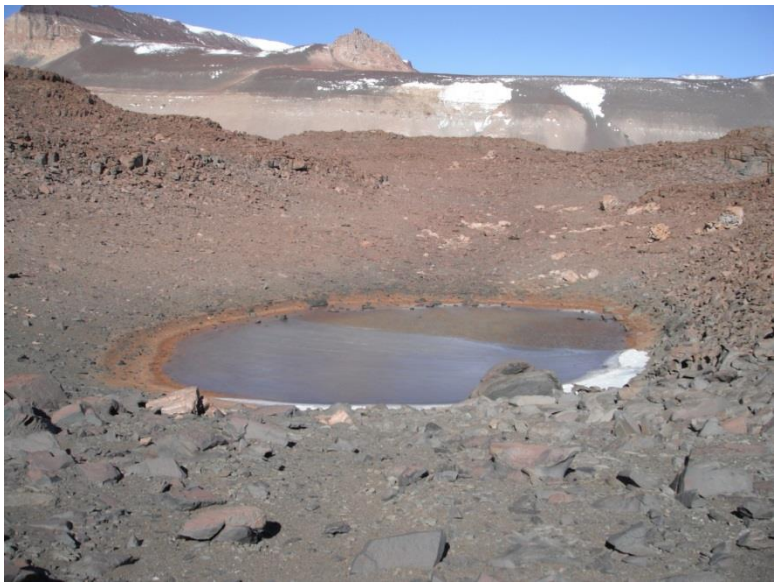


Fig. 4.5 L9A Pond in January 2012

L16 Pond

L16 pond is a large round pond that sits in the same valley, though to the north and at lower elevation than L15 (Fig. 4.6). At times of extensive melt, overflow from L15 (see map) may spill into the catchment of L16. L16 had some ice cover that decreased during the sampling period, which was mobile and moved with changes in wind direction. Microbial mats were orange near the edges, and a beige colour toward the pond centre.

Fig. 4.6 L16 Pond in January 2012

L26 Pond

L26 is a shallow round pond which was entirely ice-free at the time of sampling (Fig. 4.7). There were boulders in and around the pond, with a clearly identifiable sandstone boulder to the northwest of the pond. A comparison of photographs from this fieldwork, and that conducted by Healy (2005) showed an apparent drop in pond level between 2004 and 2012. The pond floor was covered with thin, cohesive, orange mats.

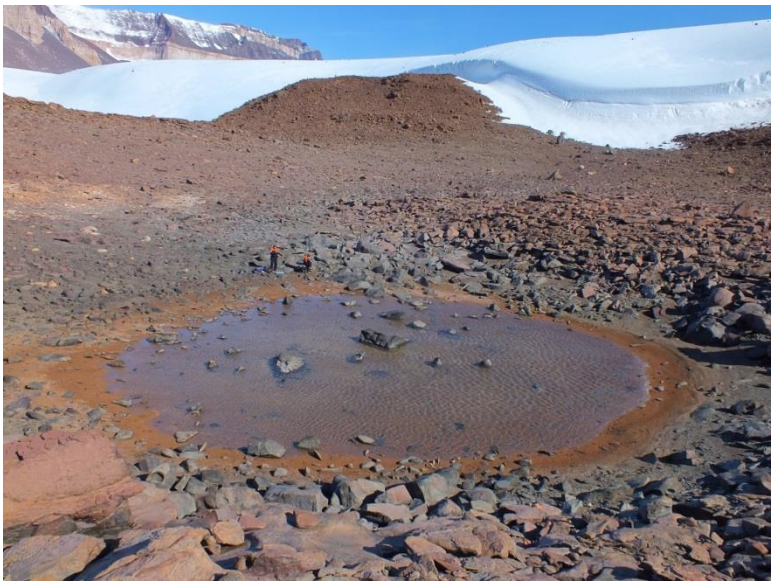


Fig. 4.7 L26 Pond in January 2012

Additional ponds in area: L15 Pond

L15 is an irregularly shaped pond that sits in the middle of a valley (Fig. 4.8). It was reported by Healy (2005) and, during the 8 years since Healy's sampling, the pond level had dropped resulting in two small basins. The larger basin had black mats and a dark green mat that appeared to be *Nostoc sp*., while the smaller basin contained only the black mat. L15 was not a principal study pond, data is presented to further inform typical pond P characteristics in the area.

Fig. 4.8 L15 Pond in January 2012

Additional ponds in area:L4 Pond

L4 pond has been previously studied, but only an empty basin was present at the time of sampling (Fig. 4.9a) (Torii *et al.* 1989, Healy *et al.* 2006). The pond was last documented to be present in January 2004 (Healy *et al.* 2006), when it was described as "a circular pond with a diameter of about 18m". The site the pond had previously occupied was obvious, and a pit was dug at the centre of the pond to sample the sediment, and to establish permafrost depth. Sampling was performed at 0-10 cm, 10-20 cm, and 20-30 cm depth. A water table was present at 30 cm depth (Fig. 4.9b), and at this stage the pit started collapsing when further attempts to deepen it were made.

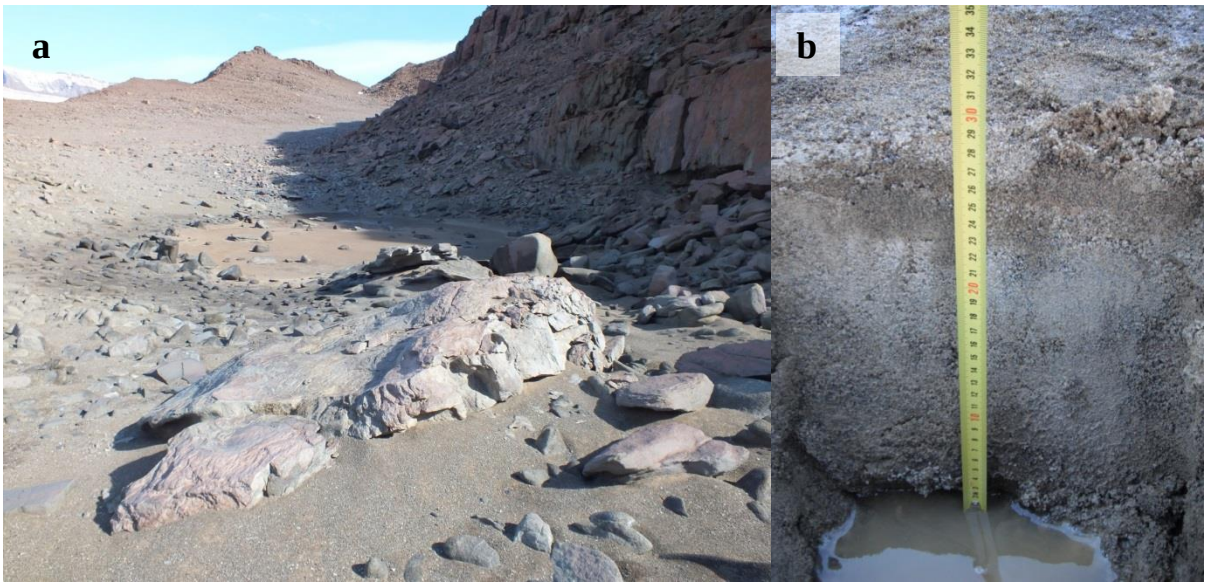


Fig. 4.9 L4 Pond in January 2012
- **a)** The dried pond basin
- **b)** The soil pit dug in the centre of the basin, with a thawed water table at 30 cm depth. White salt crystals can be seen on the soil surface.

4.3 Results

4.3.1 Pond structure and reservoir volumes

The ponds ranged in size from 18 × 20 m to 50 × 80 m (Table 4.1). Due to the large sizes of the ponds, depths were based on visual estimates and measurements from below holes made in the ice cover. For this reason, detailed bathymetry was not measured, but was visually similar to ponds at other sample sites, with pond floors following the ground relief. Depths ranged from

0.45 to 1 m. Margins of moist soil surrounded the ponds, extending 1 – 5 m beyond the pond edges (Fig. 4.3-4.8).

The depth to ice cement was not measured specifically at this site. However L4 pond was documented in 2004, and its basin was apparent. A 40 cm deep hole was dug in the centre of the basin, finding water at 30 cm (Fig. 4.9). The spade did not reach an ice barrier in the 30 cm below the water level at base of the hole. Therefore the permafrost depth below L4 was estimated at > 60 cm depth. A depth of 0.45 m to ice cement has been used for sediment and saturated soil reservoir calculations in used in this chapter for reasons discussed in section 4.4.1.

Table 4.1 Physical characteristics of the pond reservoirs, and reservoir volumes in January 2012.

Pond	**L26**	**L9A**	**L16**	**E9**	**E4**
Length (m)	20	35	70	80	80
Breadth (m)	18	18	50	50	40
Depth estimate (m)	0.45	0.55	1	1	1
Ice cover (%)	0	5	60	100	90
Mat cover (%)	100	100	100	50	100
Elevation (masl)	854	860	801	800	850
Latitude (E)	77 33 03.2	77 33 02.4	77 32 29.0	77 31 35.1	77 31 21.3
Longitude (S)	160 43 24.0	160 44 26.2	160 45 20.0	160 46 16.7	160 44 17.9
Date sampled	9-Jan-2012	9-Jan-2012	9-Jan-2012	10-Jan-2012	10-Jan-2012
Calculations of reservoir volume					
Pond water (m^3)	43	100	940	1100	940
Microbial mat (m^3)	0.6	2.8	8.5	3.3	5.7
Sediment (m^3)	130	250	1300	1500	1300
Saturated soil (m^3)	25	32	65	70	65

The volumes of the pond reservoirs were largest in E9 pond, and smallest in L26 pond. Water volumes ranged from 43 – 1100 m^3, and sediment volumes ranged from 130 – 1500 m^3. Saturated soil volumes ranged from 25 – 70 m^3, and were 5 – 19 % of the sediment volumes. The ratios of saturated soil to sediment volume were smallest in the larger ponds.

4.3.2 Pond reservoir chemistry

Water reservoir

The ponds varied in conductivity from 0.09 – 30.85 mS/cm, and in pH from 7.08 – 8.75 (Table 4.2), and did not appear correlated. Dissolved oxygen concentrations were similar, ranging from 11.48 – 12.4 mg/L. Major cation chemistry was dominated by sodium, while the dominant anion was either chloride or sulfate. Nitrate concentrations were extremely elevated in these ponds, in some cases being the second most abundant anion. TIN analysed by spectroscopic methods ranged from 3.7 – 1790 mg/L, with lowest values in E9 pond. The E9 major ion sample was lost due to tube rupture, and ion chromatography results for the remaining ponds indicated nitrate-N concentrations of 44 – 1510 mg/L, a similar range to the spectroscospy results.

Total P concentrations in the pond water were uniformly low (Table 4.2, Fig. 4.10). The one exception was L9A pond which had 181 µg/L total P. The remaining 5 ponds had 8 - 10 µg/L total P. Particulate P was the dominant P fraction in the water of all the study ponds, present at 180 µg/L in L9A pond, and concentrations of 5-8 µg/L in the other ponds. DRP and DOP concentrations for all ponds varied from below the detection limit of 1 µg/L up to 3 µg/L.

The pond water reservoir had the lowest P content of the reservoirs considered in these ecosystems (Table 4.3). Total P content ranged from 0.3 – 18 g, and was lowest the smallest pond L26, and highest in the largest pond L9A. The 3 larger ponds all had a very consistent 8-9 g of water column P.

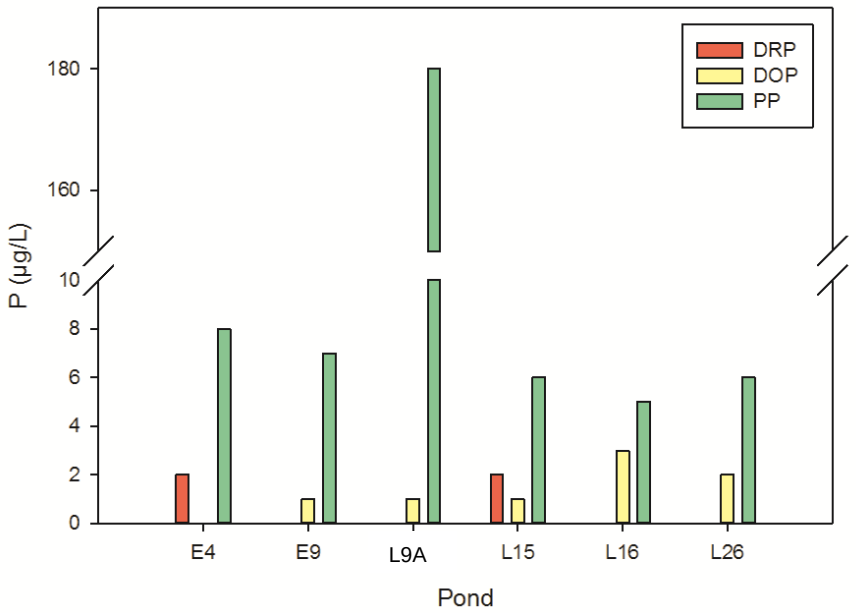


Fig. 4.10 A graph of water column P concentration and speciation. No bar represents the concentration was below the detection limit of 1 µg/L.

Table 4.2 Pond water chemical characteristics. Data is from one sample unless specified. DIN means dissolved inorganic nitrogen. The "-" symbol represents no data was collected. Values for calculations were estimated as half the detection limit where a required concentration was nondetectable.

Pond	**E4**	**E9**	**L9A**	**L16**	**L26**	**L15**
Cond (mS/cm)	1.48	0.09	30.85	4.13	29.13	1.394
pH	7.93	7.08	8.33	8.75	8.48	-
DO (mg/L)	12.4	11.68	11.85	11.73	11.48	-
TP	10	8	181	8	8	9
DRP (µg/L)	2	<1	<1	<1	<1	2
DOP (µg/L)	<1	1	1	3	2	1
PP (µg/L)	8	7	180	5	6	6
TIN (mg/L)	41	3.7	2000	227	1790	97.4
N:P (inorganic mole ratio)	0.45×10^6	0.16×10^6	88×10^6	10×10^6	79×10^6	0.11×10^6
Cl (mg/L)	226	-	12600	1316	11610	531
SO_4 (mg/L)	1161	-	1700	357	3214	1685
HCO_3 (mg/L)	27.8	2.32	427	140	689	310
NO_3 (mg/L)	397	-	7460	888	6692	397
Na (mg/L)	290	-	6198	691	5887	548
K (mg/L)	2.8	-	37.2	10.9	35.3	5.5
Mg (mg/L)	71.9	-	3516	404	3267	236
Ca (mg/L)	234	-	313	61.3	305	242

Pond microbial mat reservoir

The microbial mats varied in colour and appearance between the ponds. In E4 pond the mat was comprised of orange-brown thin matlets, which were small cohesive sections, though the mat overall was not cohesive. In E9 pond the mat was thin and sparse, beige, and was most prevalent as a covering on the gravel and stones of the pond floor. In L9A the mat was cohesive, with flaky sections on the surface, and orange-brown with a green underside. L9A had the thickest mats found in the areas ponds, and were 5 mm thick, with some sections up to 3 cm thick that were covered in bubbles. L15 pond had dark green mats that appeared to be Nostoc, as well as sections of black mat. L16 pond had mats with large flakes that were 3 mm thick, and an orange-brown colour. L26 pond had thin orange mats, that were flaky in parts, and thin sheets in other sections.

Biomass of the microbial mats ranged from 0.83 – 1.5 kg/m^2. It was highest in L15, and lowest in L9A despite the thick mats present in L9A (Table 4.4). The mass loss on ignition (LOI) however, ranged from 7.4 – 25.6 % and was highest in L9A pond, and lowest L15 (Table 4.4). The average P concentration in the mats varied from 220 – 547 mg/kg (Fig. 4.11a), and showed a correlation with LOI, highest in L9A pond, and lowest in E4 (Table 4.4, Fig. 4.11b). Interestingly, there also appeared to be a negative correlation between mat biomass and P concentration in E4 and L9A ponds ($R^2 > 0.9$, Fig. 4.11c). The mat samples from the same ponds tended to have similar P, LOI and biomass compared to mat samples from other ponds (Fig. 4.11).

The microbial mat reservoirs typically contained an order of magnitude or more P than the water column reservoir. Only in L9A pond was the P content similar, where there was high PP in the water column.

Table 4.3 Calculated values of pond reservoir P content in 2012. <dl = below detection limit.

	E4	E9	L9A	L16	L26
Water reservoir P					
Total P (kg)	0.009	0.009	0.018	0.008	0.0003
DRP (kg)	0.002	<dl	<dl	<dl	<dl
DOP (kg)	<dl	0.0001	0.0001	0.003	0.00009
PP (kg)	0.008	0.008	0.018	0.005	0.0002
Mat reservoir P					
Mat P content (kg)	0.3	0.2	1.7	0.8	0.6
Sediment reservoir P					
Total P (kg)	570	360	100	682	58
Reactive P total (kg)	43	13	3	36	8
Apatite P total (kg)	490	520	120	490	43
Porewater DRP in top 5 cm (kg)	.002	0.0004	0.0002	0.0004	0.0001
Reactive P in top 5 cm (kg)	5	1	0.4	4	0.9
Apatite P in top 5 cm (kg)	55	58	13	55	5
Saturated soil reservoir P					
Total P (kg)	17	24	13	28	12
Reactive P (kg)	2	0.8	0.5	0.6	0.3
Apatite P (kg)	15	23	13	26	11

Table 4.4 Pond microbial and substrate chemical characteristics in January 2012. na = not analysed, <dl = < detection limit.

	E4	**E9**	**L9A**	**L15**	**L16**	**L26**
Microbial mat (n=4)						
Mat biomass (kg/m^2)	1.0	na	0.83	1.5	1.4	1.3
Mat P (mg/kg)	220	na	547	335	423	425
Mass LOI (%)	7.5	na	25.6	7.4	13.5	10.5
Sediment						
Total P (mg/kg)	222	121	207	na	268	227
Pore water DRP (mg/L)	0.01	0.07	0.002	0.004	0.004	0.003
Pore water DOP (mg/L)	0.02	<dl	0.01	<dl	0.003	0.01
Reactive P (mg/kg)	17	4	7	na	14	32
Apatite P (mg/kg)	193	175	243	na	193	169
Soil						
Total P (mg/kg)	133	174	207	179	212	234
Soluble P (mg/kg)	0.009	nd	0.34	0.25	0.31	0.31
Reactive P (mg/kg)	18	6	8	14	5	7
Apatite P (mg/kg)	114	168	200	171	199	228

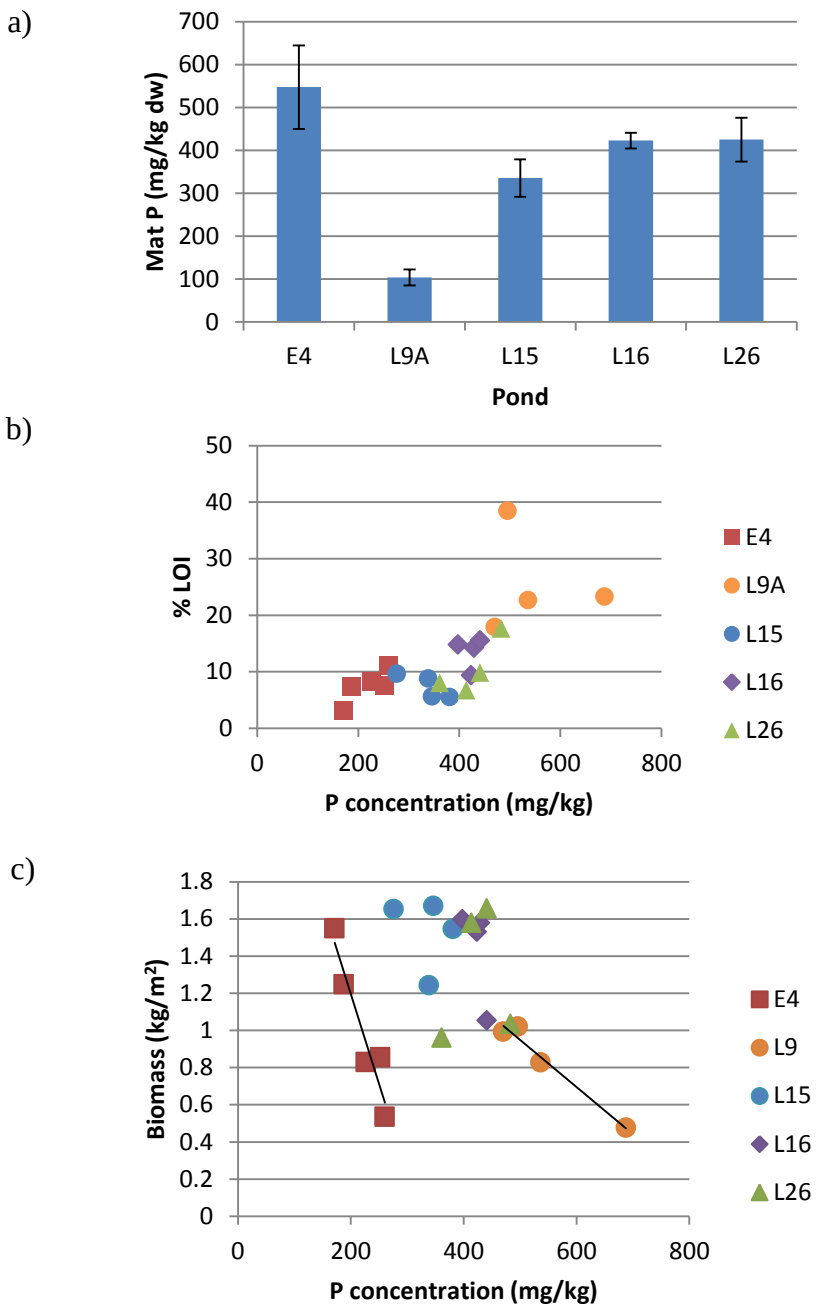


Fig. 4.11 Microbial mat P concentration, and relationships with mass loss on ignition and mat biomass.

a) Graph of the average P content in pond microbial mats. The error bars denote the standard deviation in the 4 samples analysed.

b) Mass LOI as a percentage vs P concentration (R^2 = 0.70 at E4, 0.68 at L16, 0.68 at L26, and < 0.1 at L9A and L15. For all values, R^2 = 0.19)

c) Mat biomass vs P concentration (R^2 = 0.93 at E4, 0.97 at L9A, 0.55 at L16, and <0.1 at L15 and L26. For all values, R^2 = 0.48)

Sediment reservoir

Sediments in the ponds were coarse, sandy, and typically a rich tan colour (Fig. 4.12). No sulfide smell was observed during sediment sampling. Total P concentrations in the sediments ranged from 121 – 268 mg/kg (Table 4.4). The total P content calculated to be in the sediment reservoir of the ponds ranged from 58 kg in L26 pond, to 682 kg in L16 pond (Table 4.3). This makes sediments the largest reservoir of P in the pond ecosystem, containing approximately 3 orders of magnitude more P than the microbial mat reservoir. There was no correlation between the sediment reservoir volume and total P concentration, rather, concentrations were all similar falling between 222 – 268 mg/kg, with the exception of E9 pond which had only 121 mg/kg.

Fig. 4.12 A sediment core from L26 pond, showing the tan colour of the sediment.

Sediment P was comprised principally of apatite P (84 – 97 %) in all of the study ponds. Reactive P fractions comprise the remaining 3 – 16 % of the Psenner extractable total P and were dominated by the reducible oxide P (RO-P) fraction (Fig. 4.13). The total P concentration by digestion differed from the sum of fractions in the Psenner extraction. Values were normally within 20 %, however in E9 pond the sum of the Psenner fractions was 50 % greater than the total P concentration by acid digestion.

Sediment porewater samples contained 4 – 30 µg/L of total P, lowest in L15 pond and highest in E4 pond (Table 4.4). Porewater P was dominated by DOP in E4, L9A and L26 ponds, but was present at a lower concentration than DRP in L16 pond, and was not detected in E9 and L15 ponds. In all ponds the porewater DRP concentrations were much greater than those of the overlying pond water, and where detected the DOP concentrations also exceeded the pond water levels.

Sediment cores taken from E4, L16 and L26 ponds displayed similar P concentrations and fractionations to the bulk sediment samples. The total Psenner extractable P concentration in the cores ranged from 152 – 337 mg/kg, and typically increased with depth in each pond (Fig. 4.13 a-c). Concentration ranges were similar between the ponds. Apatite P was the dominant fraction,

and RO-P was the most prevalent reactive P form. Exchangeable P was typically the smallest fraction, however in L16 pond the surface sediment, and sediments below 3 cm depth had more exchangeable P than MO-P. While the apatite-P, RO-P and the total Psenner P generally increased with depth, the exchangeable and MO-P P fractions were more variable. In all ponds, the surface sediment apatite P concentration was 30 – 40 % less than the apatite P concentration at the bottom of the core. In E4 pond the exchangeable and MO-P fractions showed some variation with depth, but not a clear trend over the length of the core. In L16 pond, a similar pattern was seen, but the exchangeable P had a zone at 1-3 cm depth that had significantly less P than the other depths sampled. L26 pond showed a trend of decreasing concentrations of exchangeable and MO-P over the length of the core.

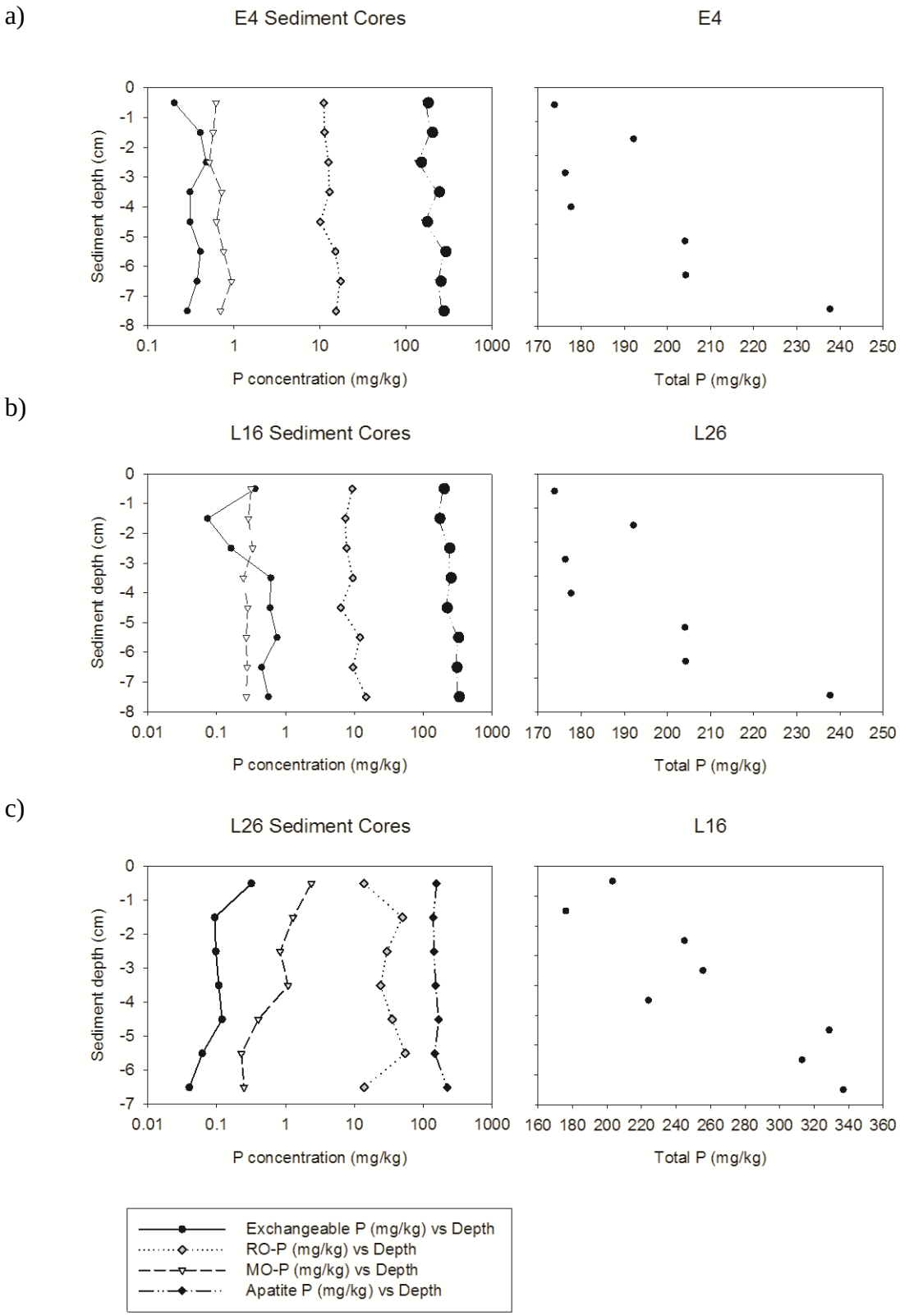


Fig. 4.13 Sediment Psenner fractionation data for cores collected from a) E4, b) L16 and c) L26 ponds.

Sediment P fractionation was consistent across the study ponds, with a general pattern of exchangeable P < MO-P < RO-P < apatite P. Concentrations of each fraction varied between ponds. Exchangeable P and MO-P varied by an order of magnitude across the 6 ponds, and also varied by a similar magnitude within the cores taken in L16 and L26 ponds. Porewater P concentrations also varied by an order of magnitude between the sample ponds. L9A pond had the lowest exchangeable P concentration.

Soil reservoir

The soils in the Upper Wright Valley appeared similar throughout the sampling area, and were typically grey-brown and sandy. The ponds occurred on the floor of the Labyrinths troughs, in areas covered in soil, with many large rocks and boulders (Fig. 4.3 - 4.9). Soil salts were visible in patches at several of the ponds. In the basin of L4 pond salts were apparent at the soil surface (Fig. 4.9).

The Hedley extraction used on soils showed a total P concentrations ranged from 133 mg/kg in E4 pond to 234 mg/kg in L26 pond (Table 4.4). The dominant form of P in soils was apatite P, which comprised 86 % to 97 % of the Hedley extractable total P (Fig. 4.14). Reactive P fractions comprised the remaining 3 to 18 %. There was very little soluble P present in the soils – with none detectable at E9 pond, and the highest concentration measured was just 0.3 mg/kg, at L9A pond. Labile P was typically the second largest fraction in four of the ponds, containing between 0.9 and 11 % of the total P. MO-P made up between 1 and 3 % of the total P, and was the second most dominant fraction in 3 of the ponds.

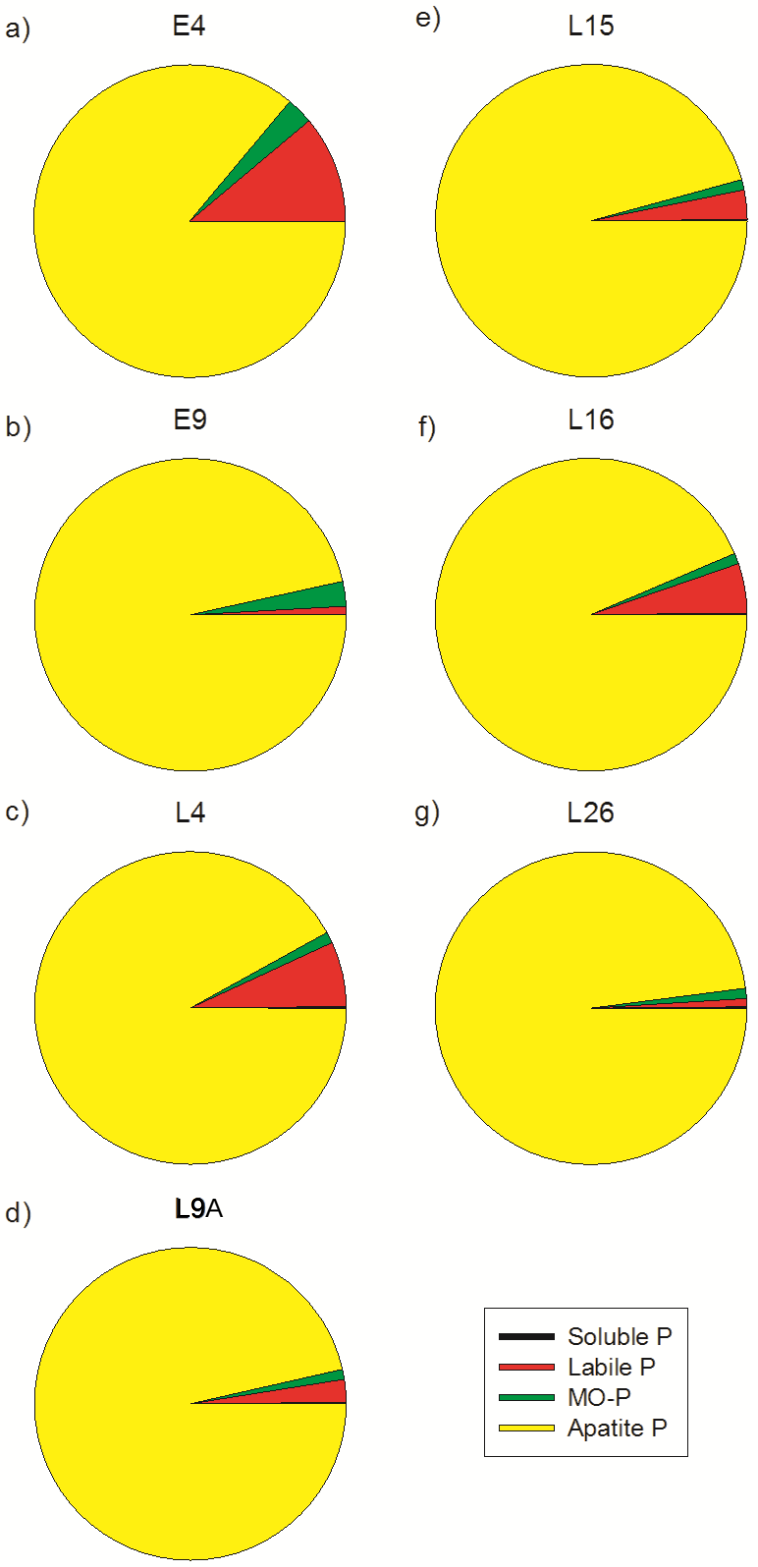


Fig. 4.14 Hedley fractionation data from soils in close proximity to the sample ponds.

The saturated soil reservoir of the study ponds contained 12 kg (L26 Pond) to 28 kg (L16 pond) of total P (Table 4.3). This makes soil the second largest reservoir of P in the ponds, with two orders of magnitude more P in the soils than in the microbial mats. There was no clear correlation between soils reservoir volume and total P concentration (Fig. 4.18).

A comparison of pond soil and sediment P concentrations and fractionations reveals similar total P, and also P fractionation in both reservoirs. Total P concentrations showed similar ranges, with 133 - 234 mg/kg in soils, and 121 – 268 mg/kg in the sediments. Across all ponds, with the exception of L15 as sediment data was not collected, the average total P concentration in soils and sediments were 192 and 209 mg/kg respectively. In some ponds sediment total P was greater than the soil total P, for example at E9 pond the sediment P had 121 mg/kg P, 30 % less than the 174 mg/kg measured in the soil. In L9A and L26 ponds the concentrations were similar in the soils and sediments, and in E4 and L16 ponds, sediment total P exceeded the soil total P by as much as 60 %. Reactive P concentrations also did not show consistent differences between the soils and sediments. In E4, E9 and L9A ponds the sediments had less reactive P than the soils, however L16 and L26 ponds had 2 to 4 times more reactive P in the sediments than the soils.

Atmospheric P sources

The snow sample that was collected from this sample site was analysed by ion chromatography. There was no detectable phosphate in the sample, and major ion chemistry was dominated by Cl^- (2.2 mg/L), NO_3^- (1.5 mg/L) and Na^+ (1.1 mg/L).

4.4 Discussion

4.4.1 P distribution and pond reservoir characteristics

The major P reservoir in all of the study ponds was the sediment, which contained 83 – 97 % of the total pond P (Table 4.3, Fig. 4.15). Around the margin of the ponds the saturated soil contained a further 3 – 17 % of pond P, and was a relatively larger reservoir in L9A and L26 which were the smallest ponds. This reflects the similar concentrations of P in soils and sediments of the ponds, and the relatively larger saturated zone surrounding the smaller ponds. The microbial mat contained a very consistent 0.2 % of pond P in all but E4 pond, where it comprised 0.1 % of pond P. The water column was the smallest reservoir of P in all ponds,

containing between 0.0004 – 0.02 % of pond P. The distribution of P between reservoirs was similar in all of the ponds.

The volume of reservoirs are constrained by the pond's physical environment. The larger ponds had larger abiotic reservoir sizes, and likely due to the larger habitat size also had larger microbial mat volumes. The magnitudes of the reservoir volumes ranged over an order of magnitude or more, while for most reservoirs the P concentrations differed by a factor of two or less. The one exception was the water column P at L9A pond, where a very high PP concentration meant the water column had 181 mg/L of TP, compared to the 8-10 mg/L measured in the other ponds. This resulted in L9A pond having the largest water column P content of all the ponds, despite having one tenth the water volume of some of the other ponds.

Photographs and field notes reveal that the ponds were significantly larger in 2004, when they were studied by Healy *et al.* (2006). L4 pond was a shallow pond at that time, and the other ponds all had higher pond levels. A drop in pond level is evident in the photos from L9A, L16 and L26, where a rim of dried microbial mat surrounds the ponds. Change in pond level at the other ponds was evident from comparison of features in the 2004 versus 2012 photographs. Torii *et al.* (1989) also reported marked changes in size of ponds in the Labyrinth, with ponds decreasing between 1977 – 1985, then increasing 'abruptly' in the 1985-86 summer season.

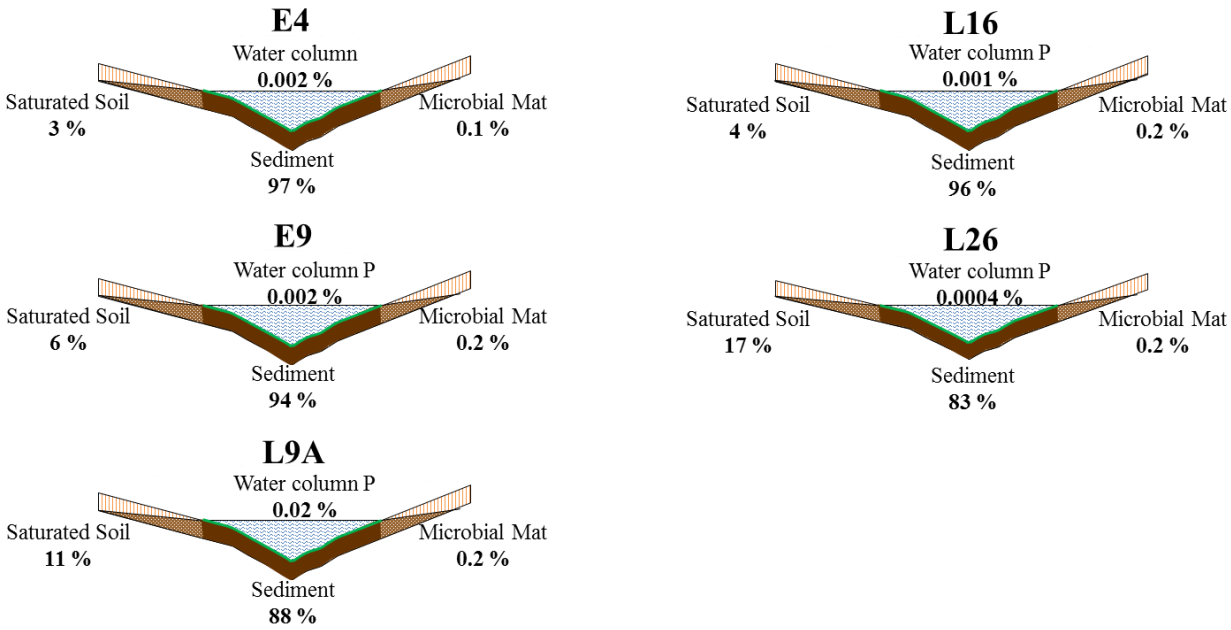


Fig. 4.15 A summary of P distribution in the reservoirs of the 6 study ponds.

The depth of the soil and sediment reservoirs has been estimated at 45 cm for these systems. The soils of the MDVs have been studied extensively over the past 50 years, and the active layer depth has been a key feature of soil characterisation. Active layers lie above permafrost, and are the zone in the soil most likely to be involved in biogeochemical cycles. Permafrost is ground that has been frozen for the preceding two years, and it is often characterized by ice cement. Permafrost with >5% moisture (ice) is generally cemented in the MDVs, and 'dry frozen permafrost' has also been documented to occur in the region (Bockheim & McLeod 2006). The Wright Upper II was a glacial advance that occurred <0.5 m.y. ago, when the terminus of the Wright Upper Glacier extended eastward 2 km beyond its present terminus (Campbell & Claridge 1987). The base of the Labyrinth within the zone covered by the advance generally has ice cemented permafrost at depths less than 50 cm (McLeod *et al.* 2009), and all seven study ponds are located in this zone. The attempt to dig to permafrost at the base of L4 pond did not reach ice cement but L4 was a dried pond, so it may not be representative for water ponds in the area. The selected depth estimate of 45 cm fell within the literature values of permafrost depth for the sampling area, and agreed with the measured permafrost depths from other sample sites studied in this thesis.

4.4.2 P speciation and availability

Water column

The water column was the smallest reservoir of P in the ponds, and contained very little DRP, the most bioavailable P form. Concentrations of DIN, particularly nitrate-N, were elevated. Consequently the ratios of DIN:DRP (Table 4.2) were well in excess of 16:1 where DRP was detected, indicating any nutrient limitation in these systems would be caused by P availability.

Ponds displayed similar fractionation of water column P species, with PP being the most prevalent fraction in all ponds. This is in contrast to ponds at Bratina Island and the large lakes of the MDVs, where DOP tends to dominate water column P with concentrations of 7 µg/L in the P limited Lake Bonney, to 780 µg/L in Salt pond on the McMurdo Ice Shelf (Dore & Priscu 2001, Sorrell *et al.* 2013, Hawes *et al.* 2014). In these other areas, DOP appears to be refractory, and able to accumulate to high concentrations. The highest conductivity ponds sampled in the Upper Wright Valley were L9A and L26 ponds, which contained 1 µg/L and 2 µg/L DOP respectively.

This suggests that, as solutes are concentrated in these ponds, DOP is not concentrated in the same way. Two possible causes for this difference are perhaps DOP is broken down more efficiently in the Upper Wright Valley ponds, or perhaps no source of refractory DOP is present in this area. PP in the water column may be planktonic, mineral phases, or organic detritus, but was not characterized for this study. L9A pond had anomalously high PP concentrations, causing the size of the water reservoir to be much greater than in the other ponds (Fig. 4.15). High PP in L9A, together with the high mat LOI and P content, seems to indicate greater acquisition of pond P by the biological components of the pond.

Microbial Mat

The microbial mat is a minor reservoir of P in the ponds, containing 0.1 – 0.2% of pond P. However, the mat is important as the major biomass of the system, and as source of recyclable P. Microbial mats are capable of accumulating P to concentrations more than double the total P concentration in sediments. Microbial mats that grow on sediments invariably contain fine sediment grains within the mucilaginous matrix of the mat, which can adsorb high concentrations of trace metals (Fig. 4.16)(Webster-Brown & Webster 2007). The metal oxides which are proficient at binding trace metal ions, often have high affinity for phosphate (Cornell & Schwertmann 2003). The measurement of mat P includes all of the living, mucilaginous, detrital organic and mineral P in the mat sample, and it is difficult to attribute the P to a biological or mineral form in the mat. However, the apparent trend of increasing % LOI with increasing P content indicates more organic matter is present in the mat samples with highest P (Fig. 4.11 b). Additionally, higher biomass samples had lower P content (Fig. 4.11 c). Biomass was measured as the dried weight of the mat, and the samples from L9A pond with the thickest mats had some of the lowest weights. Therefore the higher biomass samples likely included greater proportions of entrained sediment. The higher P content in the lower biomass samples suggests that mat P is predominantly in biological component of these samples.

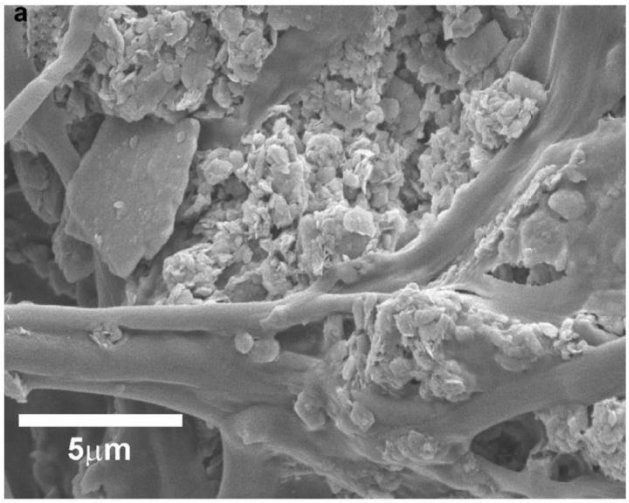


Fig. 4.16 Scanning electron microscope image of air-dried microbial mat sampled from Lake Vanda in the Wright Valley. Image copied from Webster-Brown and Webster (2007), and shows entrainment of fine sediments in the microbial mat matrix.

Microbial mats can act as a source, sink, and possible barrier for P transfer in meltwater ponds. Microbial mats sequester P from overlying water, and can also release P to the water, particularly in association with freeze-thaw events (Howard-Williams *et al.* 1997, Hawes & Howard-Williams 1998). 'Lift off' events, where sections of mat detach from the pond floor, in ponds from the McMurdo Ice Shelf can cause substantial nutrient release, suggesting the mucilaginous matrices of mats act as a barrier to diffusion (Hawes *et al.* 1993). In contrast to the thick and cohesive McMurdo Ice Shelf pond mats, the mats in the Upper Wright Valley were often flaky and thin, and, except for L9A pond, were only cohesive in sections. The drivers and mechanisms of the structure of microbial mats are a current topic of research (Hawes *et al.* 2011). Flakey mats have a higher surface area which may facilitate nutrient uptake in low concentration systems, and could allow for greater exchange between sediment porewater and pondwater solutes via diffusion, compared with a cohesive mat.

Sediment

Sediments are the major reservoir of P in the Upper Wright Valley ponds, however very little of the total P is in a form available to pond biota. The P in the sediments was dominated by apatite P, which comprised 84 – 97 % of the Psenner extractable P.

The exchangeable, RO-P and MO-P fractions are the most reactive fractions targeted by the Psenner extraction used for the sediments (Psenner *et al.* 1988). Exchangeable P may be released by ion exchange, so it is logical for E4 and E9 ponds, which had the highest exchangeable P, to also have the highest porewater P concentrations. RO-P is adsorbed to redox sensitive metal oxides, and can be released under reducing conditions that react with and dissolve the metal oxide (Psenner *et al.* 1988). These oxides often have large surface areas and an affinity for phosphate ions. There was no indication of reducing conditions present in the ponds, with no hydrogen sulfide smell apparent during sampling, and all sediments being a rich tan colour, typical of iron III oxides.

The sediment cores showed varying results, which may reflect different processes occurring in each pond. The apatite P fraction behaved similarly in all of the cores, increasing with depth by 30 % or more from the surface to the bottom of the core. This increase with depth was also observed in the RO-P fractions in E4 and L16 ponds, and a more variable trend was seen in the exchangeable and MO-P fractions. This may reflect increased weathering and transport of P in the sediments closer to the surface. L26 pond had several different results. The surface sediment, and the sediment at 6-7 cm depth had low RO-P concentrations. Reducing conditions have not been documented in these ponds, and were not noted at the time of sampling. However, reduced dissolved oxygen concentrations of 7 mg/L were measured in October 2004. It is likely that localized reducing conditions may develop in the basal brine at the pond centre over winter, however it is possible in the rest of the pond sediments remain oxygenated. Reducing conditions should be further investigated as a reason there may be low RO-P directly beneath the microbial mat in this pond. The MO-P and exchangeable P concentrations were markedly different, and both decreased with depth in the core. This may be due to recycling of mat material in the surface sediments [and is similar to the trends seen in McMurdo Ice Shelf ponds (Chapter 3)].

The apatite P fraction in the sediments includes P in the form of apatite, and P associated with calcium or within acid soluble crystalline metal oxides. This fraction is generally considered to be only slowly available, requiring chemical weathering to break it down into a free phosphate form. In ponds at the McMurdo Ice Shelf (Chapter 3), and in streams of the Taylor Valley (Bate *et al.* 2008) however, there is apparent loss of the apatite P fraction in sediments relative to soils. The increase in apatite P concentration with depth in the sediment cores supports that this

fraction is available to the ponds by a similar mechanism. However; the Upper Wright Valley soils and sediments have similar apatite P concentrations, with sediments sometimes having higher apatite P concentrations than the surrounding soils. This will be further explored in the following soil section.

Soils

Saturated soils were the second largest reservoir of P in the ponds, but are likely to provide less P available to the ponds than sediment. The majority of soil P is present as apatite P, and requires weathering to become available, and additionally requires transport through the soils and sediments to reach the pond, either by diffusion or ground water flow.

Soils had remarkably similar total and reactive P concentrations to the pond sediments. E9 pond had 30 % less total P in the sediments than the soils, however this indicates heterogeneity rather than P loss from the sediment relative to the soil, as soils at other ponds have less P than sediments by a similar magnitude. The mean concentrations of total P for soils and sediments were within 1 standard deviation of one another. Due to the documented changes that occur in pond level in this area, it is likely that the soils have been flooded from time to time (Torii *et al.* 1989).

The soils sampled near the Labyrinth ponds had lower P concentrations than those reported for soils not associated with ponds at other locations in the MDVs. Soils throughout the Dry Valleys have derived from a variety of parent material, including sandstone, granite, dolerite and basalt. Bate *et al.* (2008) used a very similar sequential extraction as was used in this study, to determine phosphorus distribution in soils of the MDVs. Soil samples were taken from Ross Sea drift soils near Lake Fryxell, Taylor II drift soils in the Lake Hoare, Lake Bonney and Bonny Riegel areas of the Taylor Valley, and from the Pearse, Beacon and Lower Arena Valleys. Soil phosphorus was dominated by apatite P, comprising over 90 % of the soil P at all sites but Lake Fryxell. This was also the dominant fraction of P in the Upper Wright Valley soils as shown in this study. Interestingly, comparison of the average apatite P concentration in the Upper Wright Valley soils (180 mg/kg), with those of other areas in the MDVs reveals concentrations of P in the Upper Wright Valley soils have approximately 30 % less P than soils from the other inland dry valley sites (Fig. 4.17). The deeper sediments in the cores had concentrations of 223 – 337

mg/kg P, which is more comparable to the inland soils reported by Bate *et al.* (2008). The Labyrinth is an old feature, formed by subglacial water flow (Lewis *et al.* 2006). In the Labyrinth, the dominant bedrock is Ferrar Dolerite, which intrudes the Beacon Supergroup Sandstones throughout the Dry Valleys area (Campbell & Claridge 1987, McLeod *et al.* 2009). The similarity of P concentration and speciation in surface soils and sediments in the Upper Wright Valley, together with the higher concentrations of P in deeper sediments, suggests that the soils sampled for this study have been subject to flooding and similar weathering to the sediments sampled. It is therefore apparent that sediments do contribute P to the ponds through weathering of apatite minerals, and that submerged soils also behave in this way.

The low concentrations of the surface soils and sediments relative to the deeper sediments suggest loss of P over time. In L16 pond, the total P concentration calculated to be in the top 5 cm of soil using the average concentration of sediments at 0-5 cm depth (220 mg/kg Psenner extractable P), is 62 kg of P. The same calculation using the concentration from the bottom sediment in the core of 336 mg/kg P, is 95 kg. This indicates that over the lifetime of the pond, a value in the order of 30 kg of P may have been transferred from the sediments to the mat and water column. This value is much greater than the P presently in the mats and water column of L16 pond, and is likely due to P loss with biomass loss during periods of dessication.

The low soluble P concentrations (ranging from below detection – 0.3 mg/kg) indicate that reflooding of the soils may release only a small amount of immediately available P to the ponds. Further sampling will be required to establish the nature of P in soils that have not been flooded, and the potential effect of their flooding on pond P. Use of transects, as has been performed in other chapters of this thesis may help to establish the boundaries of previous floodings. If soil P concentrations and speciation in the inland Dry Valley sites reported by Bate *et al.* (2008) are representative of the Upper Wright Valley soils, it is unlikely that flooding of these soils will cause significant available P to be rapidly released.

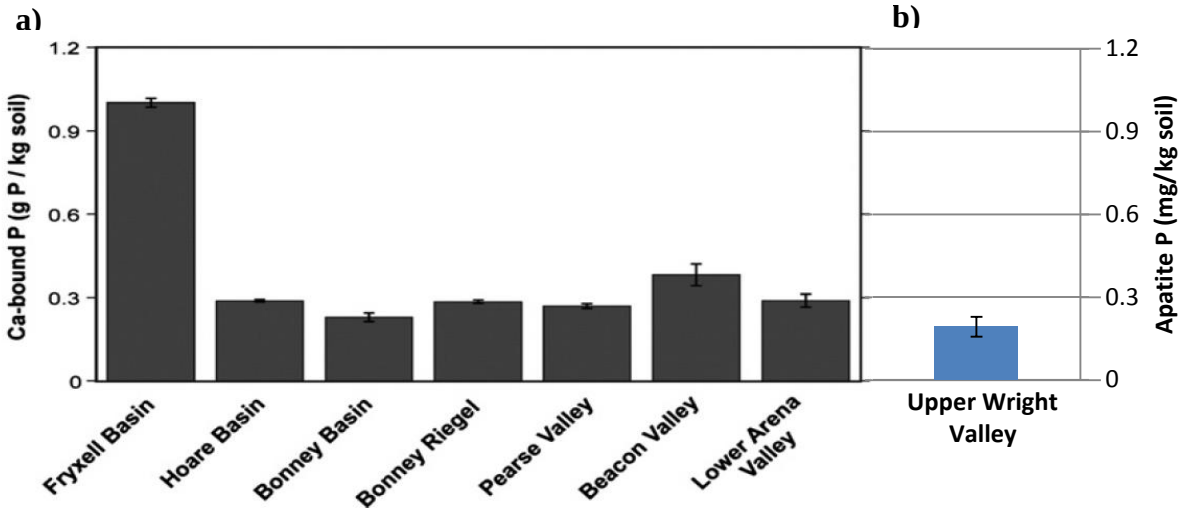


Fig. 4.17 Comparison of soil apatite P concentration in McMurdo Dry Valley soils

c) Average apatite P concentrations for several sample sites in the McMurdo Dry Valleys, modified from Bate *et al.* (2008). In this study an almost identical sequential extraction to the one used in this study was performed, allowing direct comparison of the apatite P fractions between these two studies.

d) The average apatite P concentration from the Upper Wright Valley soils.

4.4.3 A P model for inland ponds

The ponds selected for this study covered the range of conductivities seen in a survey of ponds in the area prior to sampling. Major ion composition of the ponds, with sodium chloride dominance, with high sulfate and nitrate concentrations relative to seawater are comparable to previous studies for the area (Torii *et al.* 1989, Healy *et al.* 2006). The soil and sediment P concentrations are lower than, but in a comparable range to those of other inland areas in the Dry Valleys (Bate *et al.* 2008), and with sediments acting as the major source of P to the ponds, it is likely that ponds on sediments with similar P fractionation will have similar P dynamics.

This chapter has not addressed possible chemical stratification of the ponds, which does occur in the area (Healy *et al.* 2006). Such stratification is caused by cryoconcentration of solutes at the base of ponds, which can persist on thawing if the water column remains undisturbed. In January 2004, Healy (2005, 2006) measured conductivity stratification of 14 ponds in the Upper Wright Valley. Where stratification was present, it typically occurred in the bottom 5-20 cm of the pond. Basal conductivities ranged from 0.127 – 72 mS/cm. For this present study, the ponds were typically too large to sample the base at the centre, though a green brine which can be typical of

stratified ponds in coastal areas was not observed (Wait *et al.* 2009). At Bratina Island, stratified ponds had increased DRP and TP concentrations at the base, with at least one pond where TP concentration correlated to conductivity (Chapter 3). If a similar relationship exists in ponds of the Upper Wright Valley, it is possible that the model above has underestimated the P content of the water reservoir. In Huey pond at Bratina Island, using a surface P concentration only to calculate the water reservoir content resulted in a value 14 % less than if stratification was considered. Due to the very low P concentrations in the pond waters of Upper Wright Valley, even if a similar, stratified distribution of P occurs in the water column of ponds, the water column will still be a very small reservoir of P in these systems. Therefore, the model is likely to predict P distribution in most ponds in the Labyrinth area. Additionally, if soils in the Upper Wright Valley that are not adjacent to ponds are similar to those of other inland dry valley areas, the model is likely to predict P distribution in these areas as well.

4.5 Summary

This chapter characterizes P in the ponds of the Upper Wright Valley. The ponds studied are inland systems with high N:P ratios, indicating nutrient limitation by P availability.

Key findings:

- The ponds contain very little DRP in the water column, and have inorganic N:P ratios indicative of a P limited system.
- Pond P is predominantly held in the sediment reservoir, with soils being the second major reservoir. Microbial mat contains 0.04-0.05% of total pond P, and the water column is the smallest reservoir.
- In both soils and sediments, apatite P is the dominant P form, and <0.2 % P is readily available to be dissolved. Sediment cores suggest that the apatite fraction can be made available to the pond, via weathering and transport, over long time periods. P associated with reducible oxides are the second dominant P form in sediments, with labile P the second dominant form in soils.
- Soils close to the ponds contain low apatite P concentrations relative to other McMurdo Dry Valley soils that have been studied, likely due to weathering of apatite minerals when pond levels were higher.

Chapter 5:
P distribution in other key ponds of the Victoria Land region, Antarctica

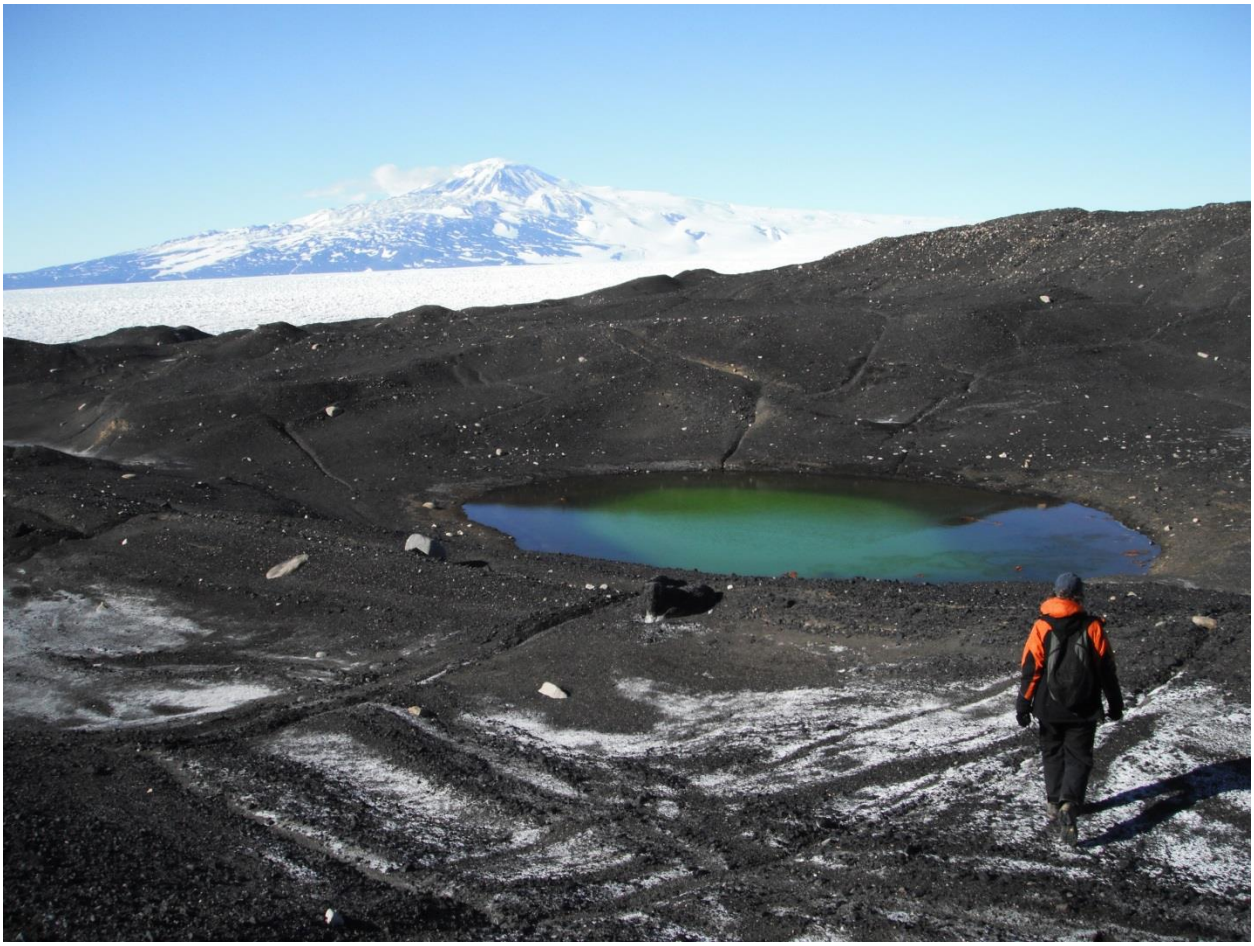


Fig. 5.1 An image of a pond in the Miers Valley mouth, with soil salts visible in the foreground, and the Koetlittz Glaicer and Mt Discovery in the background.

5.1 Introduction

Chapters 3 and 4 in this thesis have established the abundance of P in the different reservoirs of ponds both in the coastal system on the McMurdo Ice Shelf, and the inland system of the Upper Wright Valley. Phosphorus abundance at these two sites supported established ideas of nutrient availability (Vincent & Howard-Williams 1994). Low N:P ratios were demonstrated on the McMurdo Ice Shelf, in contrast to high N:P ratios found in the Upper Wright Valley. Similar patterns of P distribution were seen in both systems, with sediments being the principal P reservoir, followed by saturated soil, with the microbial mat and water column holding very little pond P. Sediments were identified as the major source of P to the pond in both systems.

The example ecosystems studied in the preceding two chapters represent extremes of the coastal and inland ecosystems of Victoria Land. There are numerous systems which fall at an intermediate distance from the coast, and at coastal areas on different geologic settings, which will be described in this chapter.

Contribution of this research

This chapter addresses research questions 1.3.1 and 1.3.2 as outlined in Chapter 1, by determining P distribution and P sources for ponds of the Lower Wright Valley, the Miers Valley, and Ross Island. The Lower Wright and Miers Valley systems represent 'intermediate' settings, where the sites are not adjacent to the coast, but may still receive some coastal influence via aerosols. The Ross Island sites are directly adjacent to the Ross Sea, and occur on the flanks of volcanic Mt Erebus. The abundance and speciation of P in the reservoirs of up to 6 ponds at each of the sample sites have been identified.

5.1.1 Chapter objectives

This chapter aims to characterize P in ponds from 3 different areas in the Ross Sea region, and to establish whether models produced for McMurdo Ice Shelf and Upper Wright Valley ponds can be applied to P distribution in those 3 areas. These aims will be achieved by:

- Establishing distribution of P in each of the ecosystems
- Determining speciation of P in each of the main reservoirs
- Identifying sources of P to the ponds

5.2 Site descriptions

5.2.1 Lower Wright Valley

The McMurdo Dry Valleys are a series of ice free valleys to the west of McMurdo Sound in Southern Victoria Land. The Wright Valley, as described in Chapter 4 is east-west oriented, and the Lower Wright Valley sampling area was at the eastern end of the Wright Valley, in the vicinity of proglacial Lake Brownworth and the head of the Onyx River (Fig. 5.2). The Wright Lower Glacier, a lobe of the Wilson Piedmont Glacier fills the valley mouth. Bedrock in the east and central Wright Valley comprises Skelton Group metasediments, consisting of marbles, hornfelses and schists, as well as Wright intrusives of granite-gniesses (McKelvey & Webb 1962). The valley floor is covered by moraine and fluvioglacial deposits (McKelvey & Webb 1962).

The glacial deposits in the Wright Valley are from three sources. An outlet glacier of the East Antarctic Ice Sheet (EAIS) cut the valley, and the oldest till in the valley is from a similar wet based glacier that filled the valley, draining the EAIS before 3.9 Ma (Prentice *et al.* 1993). On at least 8 occasions, grounded ice from the Ross Sea Embayment has advanced westward into the Wright Valley, advancing the Wright Lower Glacier up to 21 km west of its present terminus (Hall & Denton 2005), and it is this till that covers the area sampled in this study. Several alpine glaciers also exist further west of the study site, which have deposited tills into the valley.

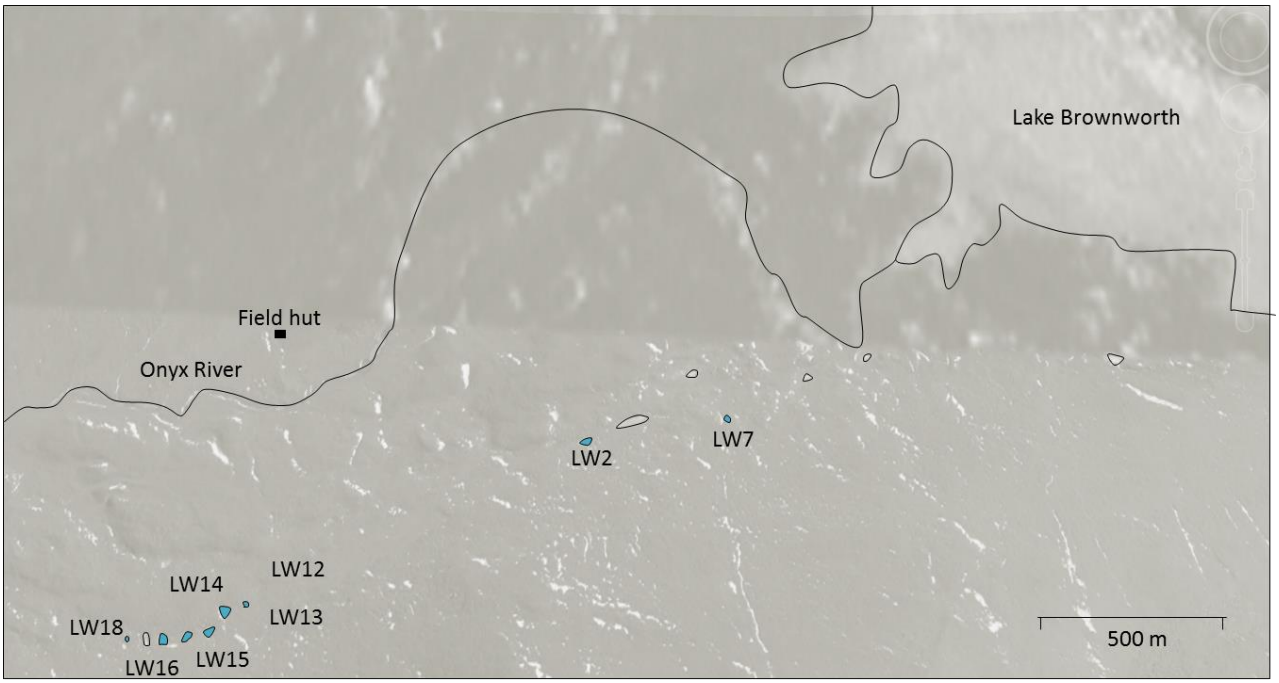


Fig. 5.2 Map of the Lower Wright Valley sampling area, overlying an image of the sampling area taken from Google Earth (Image date 16/11/2008). The ponds sampled for this study are coloured blue, and other major features and obvious pond systems are outlined.

The study area was south of the Onyx River, where numerous ponds occur on the valley floor in topographical depressions. The majority of the ponds had snow banks, which are the most likely source of their nourishment.

5.2.2 Miers Valley

The Miers Valley is an ice free valley in the Keottlitz region of Victoria Land. It sits in the eastern foothills of the Royal Society Range, bound by the range to the west, and sloping eastwards to the valley mouth at the Koettlitz Glacier. The sides of the valley are bound by bedrock ridges up to 800 m in elevation. The valley ranges from 1.5 to 2.5 km in width, and is 11 km in length. Two alpine glaciers occur at the head of the valley. The exposed bedrock in the Miers Valley is Precambrian marble and schist, with some granite intrusions through the valley walls (Blank *et al.* 1963). The valley floor is covered by Cenozoic moraines, and quaternary fluvio-glacial, lacustrine and deltaic deposits (Blank *et al.* 1963).

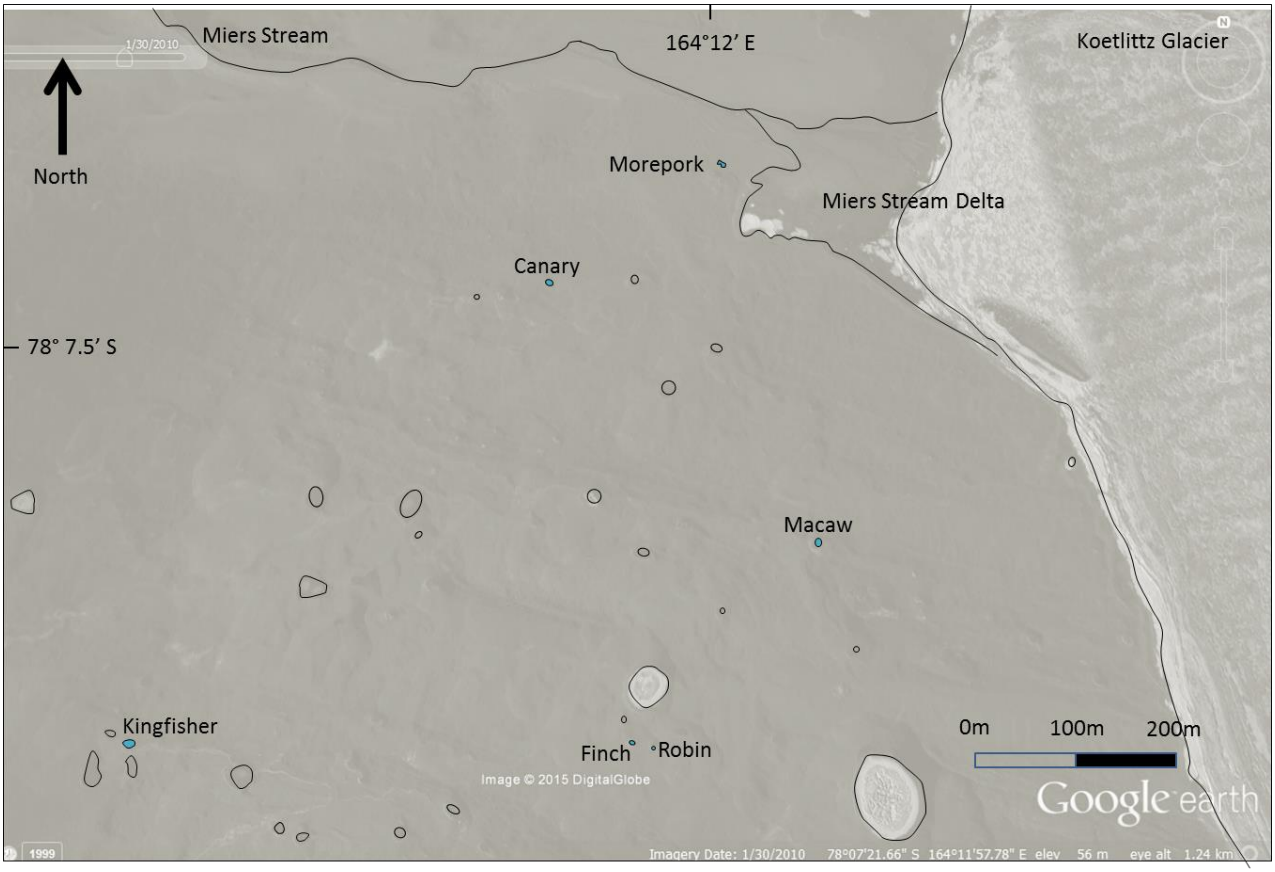


Fig. 5.3 Map of the Miers Valley sampling area, overlying an image of the sampling area taken from Google Earth (Image date 30/1/2010)). The ponds sampled for this study are coloured blue, and other major features and obvious pond systems are outlined.

The study area was at the Miers Valley mouth (Fig. 2.2), on ice-cored moraine that was deposited in the last glacial maximum (LGM). During the LGM a grounded ice sheet existed in McMurdo Sound that was fed from the Ross Embayment. The ice flowed inland and westward from Ross Island into the coastal dry valleys including the Miers Valley, and deposited the Ross Sea drift sheet (Denton & Marchant 2000). The drift is matrix supported, with erratics including volcanics transported from Ross Island, as well as cobbles of granite, dolerite and sandstone (Denton & Marchant 2000). This drift blankets the coastal headlands and Miers Valley mouth to an elevation of 250-260 m. The valley floor is covered in a glacio-lacustrine drift that was deposited by a 'lake ice conveyer' from ice moving on the surface of the Glacial Lake Trowbridge, that formed when the valley mouth was dammed by a lobe of the Ross Ice Sheet (Clayton-Greene *et al.* 1988, Denton & Marchant 2000).

In the upland region of the valley, meltwater from the two alpine glaciers feeds Lake Miers, which is drained by the Miers stream. The stream drains to the Koettlittz Glacier in the Miers Mouth.

The study area was to the south of Miers Stream (Fig. 5.3). Morepork pond was in a depression on the valley floor, within several hundred meters of the streams delta. The remaining study ponds were selected from the numerous meltwater ponds that occur in the undulating terrain on the southern slope of the valley mouth. At the start of the sampling period no snow banks were present near the ponds, however a snowfall event during sampling deposited snow in the catchments of all the ponds, and snow is likely to be the major meltwater source to these ponds.

5.2.3 Ross Island

Ross Island consists of 4 stratovolcanoes in the Ross Sea off the coast of Victoria Land and bordering the northern edge of the Ross Ice Shelf (Fig. 2.2). The lavas that make up the island are predominantly alkaline basalt and differentiates (Kyle & Cole 1974). The island is predominantly ice-covered, though areas of bare ground occur at a number of locations on the coast. Meltwater ponds in these ice free areas have been of scientific interest since the very first expeditions to Ross Island, and those at Hut Point Peninsula, Cape Royds, and Cape Evans have been studied in this thesis. Most of the Ross Island study ponds had snow accumulations nearby, which is likely the dominant source of their meltwater.

Hut Point Peninsula

Hut Point Peninsula protrudes 20 km south west from the slopes of Mt Erebus on Ross Island. The peninsula was formed by volcanic activity between 0.4 and 1.2 million years ago, and is comprised of a series of volcanic cones comprised of basanite, basanitoid, phonolite and hawaiite lavas (Kyle & Treves 1974). The peninsula has a three pronged head (Fig. 5.4). Observation Hill sits on the central prong, and the northern prong is Hut Point. The embayment between these points contains McMurdo Station, the United States Antarctic Programme's main base. The southern prong of the peninsula is Pram Point, and the location of the New Zealand Antarctic Programme's Scott Base. Hut Point is also the site of the hut built by the 1901-1904 British National Antarctic Expedition.

Numerous meltwater ponds exist near Hut Point, and one pond is present on Observation Hill. Both of these areas have recreational walking tracks that are used by people visiting the two bases in the area. Two study ponds were selected for this work, the pond on the slopes of Observation Hill, and one pond at Hut Point.

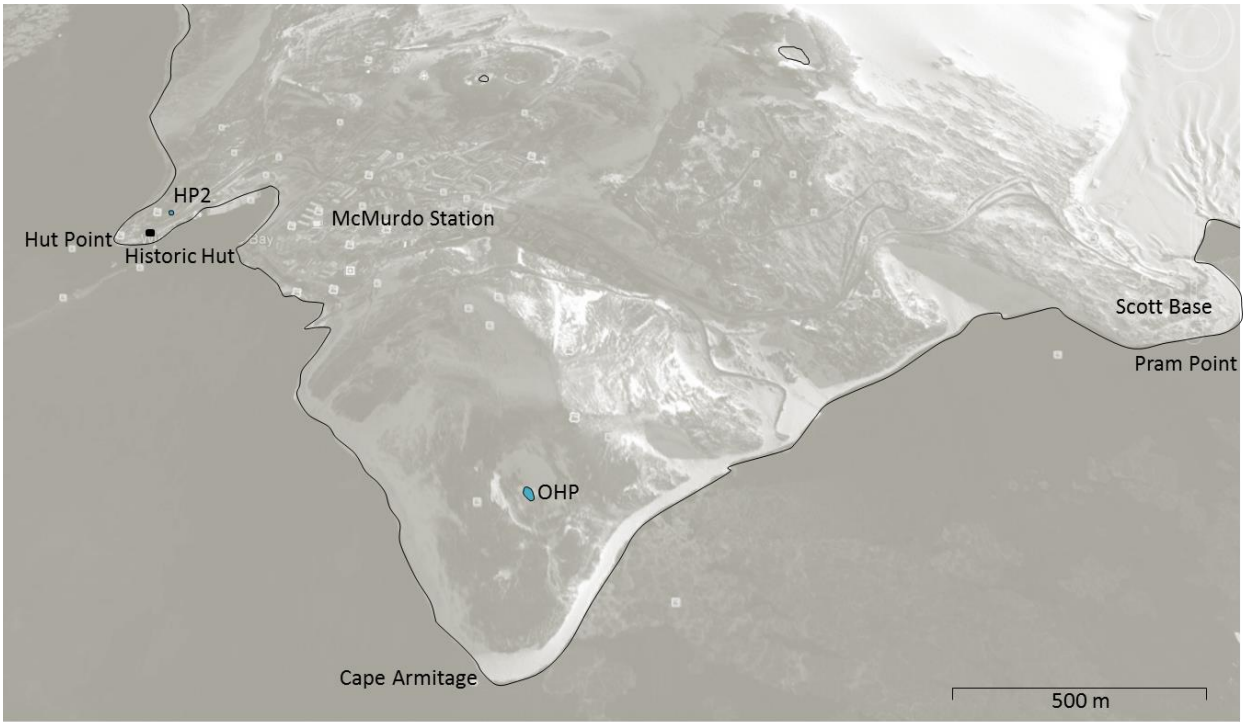


Fig. 5.4 Map of the Hut Point Peninsula sampling area, overlying an image of the sampling area taken from Google Earth (Image date 5/3/2011). The ponds sampled for this study are coloured blue, and other major features and obvious pond systems are outlined

Cape Royds

Cape Royds is the westernmost point of Ross Island, on the Flank of Mt Erebus (Fig. 5.5). The bedrock is volcanic, predominantly kenyte, a differentiate of an olivine basalt (Treves 1962). Morainal material is abundant, in some areas completely covering the bedrock, and marine mud has been reported at 180 feet elevation (Treves 1962). Erratics are common, and include igneous, sedimentary and metamorphic rocks, and rocks along the shoreline have mirabilite crusts (Treves 1962).

Numerous lakes and ponds occur near Cape Royds, and were first reported by members of the 1907-1920 British Antarctic Expedition (David *et al.* 1914). Two lakes and a pond in the area were studied by Vincent and Vincent (1982) and had inorganic N:P ratios below the Redfield ratio, indicating possible N limitation. Enrichment studies showed no planktonic uptake of P following enrichment.

Cape Royds is home to an adelie penguin rookery with ca 2000 breeding pairs, and many skua also inhabit the area (Broady 1989). Skua nest around some of the ponds, and both skua and penguins have been observed swimming and bathing in some of the large ponds in the area.

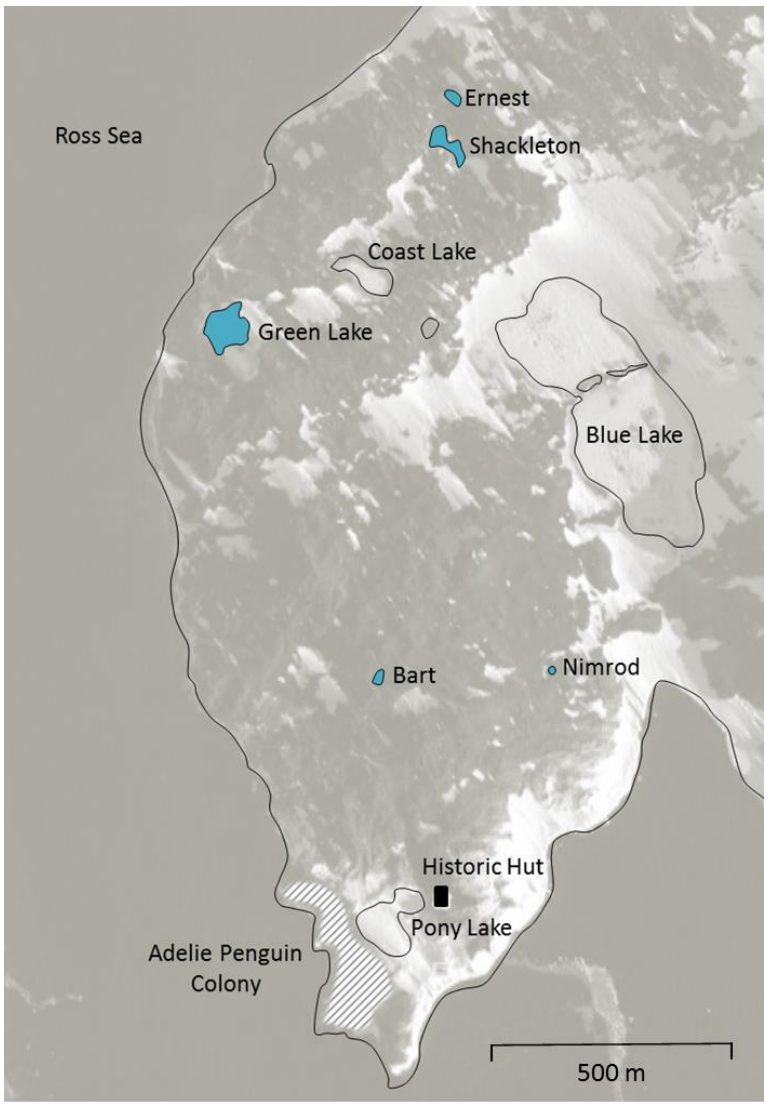


Fig. 5.5 Map of the Cape Royds sampling area, overlying an image of the sampling area taken from Google Earth (Image date 24/2/2011). The ponds sampled for this study are coloured blue, and other major features and obvious pond systems are outlined.

Cape Evans

Cape Evans is also located on the western coast of Ross Island, 12 km south of Cape Royds. Geology at Cape Evans is dominated by kenyte very similar to that at Cape Royds (Treves 1962). The topography at Cape Evans is undulating, with an estimated relief of 60 m. Numerous ponds are present in the depressions, and are commonly associated with snow banks (Fig. 5.6).

About 10 breeding pairs of skua were nesting in the area, and penguins were observed near the ponds, but do not breed in the area.

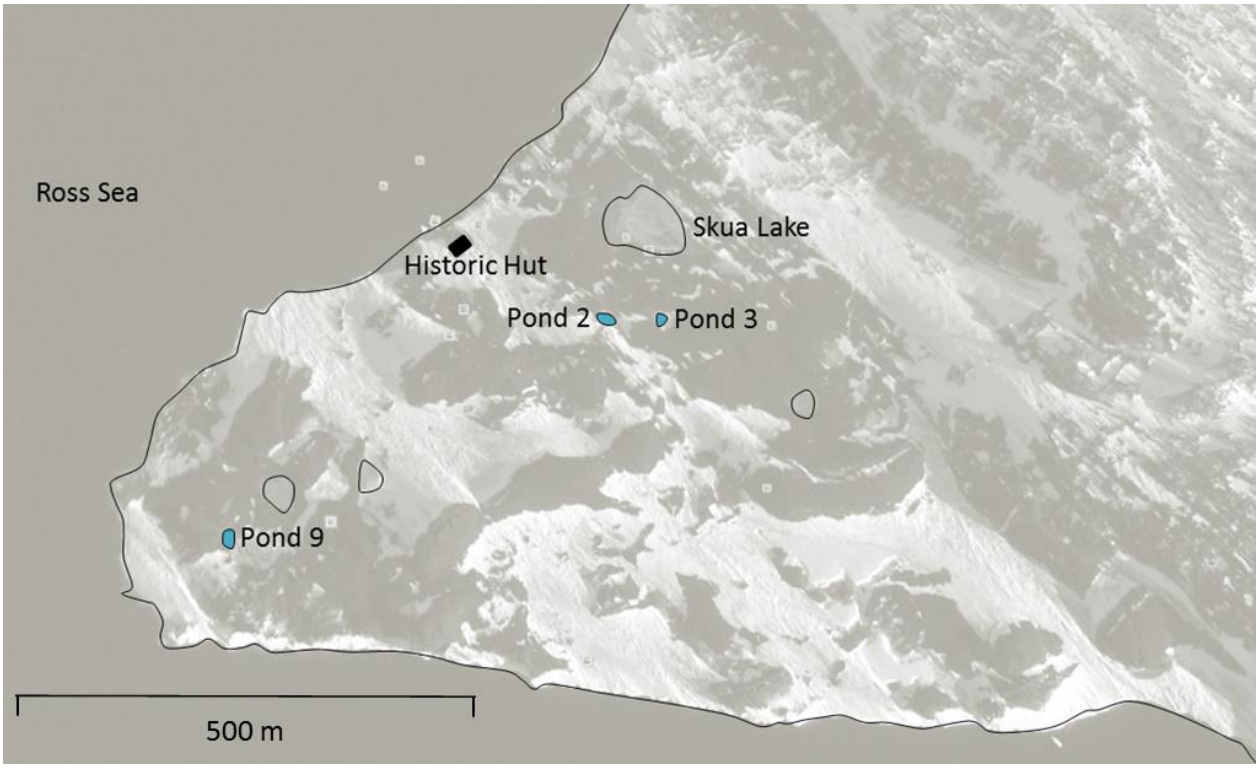


Fig. 5.6 Map of the Cape Evans sampling area, overlying an image of the sampling area taken from Google Earth (Image date 24/2/2011). The ponds sampled for this study are coloured blue, and other major features and obvious pond systems are outlined.

5.2.4 Methods at each study site

As described in Chapter two, the sets of samples and data taken at each of these sample sites differed slightly.

5.2.5 Pond descriptions

Twenty four ponds of varying sizes were selected from the 5 sample sites according to the selection criteria outlined in Chapter 2 (Table 5.1).

Lower Wright Valley pond descriptions

LW2

LW2 was an elliptical pond with cohesive orange mats covering the pond floor (Fig. 5.7 a). At the southwest side of the pond however, the mats appeared duller, which was attributed to a covering of dust. The pond appeared to have decreased in size recently, evidenced by exposed mats. No ice cover or snow bank was present, however a salt margin around the pond and patches of soils salts were present in the catchment.

LW7

LW7 was an elliptical pond with black mats. This was not a principal study pond in the Lower Wright Valley, but some data is presented to give a more complete picture of typical pond characteristics in the area. No ice cover or snow bank was present in the catchment. There was a channel out of L7, suggesting intermittent drainage to a neighbouring pond.

LW12

LW12 was a round pond with cohesive orange mats. This pond was also not fully sampled as a study pond. The data presented complements other work on this pond, and gives a broader view of P characteristics of ponds in the area. The pond had no ice, and 3 very small snow accumulations. Soil salts were present in the catchment.

LW13

LW13 was a clear pond with a cohesive orange mat. Thin ice covered most of the pond surface, and a snow bank was present. A sulfide smell was noted when sediment was sampled from this pond.

LW14

LW14 was a narrow, shallow pond that had a cohesive mat. The mat cross section had orange and green layers. The pond had no snow banks, and had 50 % thin ice cover.

a) b)

Fig. 5.7 Images of ponds from the Lower Wright Valley
a) LW2 Pond b) LW15 Pond

LW15

LW15 was a rectangular pond with snow banks on opposite sides (Fig. 5.7 b). The exposed sides had considerable soil salt accumulations. Thick orange lift off mats occurred at the ponds centre, and at the edges a crusty mat was present. The pond had 90 % ice cover at the time of sampling.

LW16

LW16 pond was an elliptical pond that was completely covered by 9 cm thick ice. Two snow banks were present at the pond edge. The pond floor was covered by mats, with areas that were orange with small pinnacle structures, and were crusty and thin over gravel in other places.

LW18

LW18 was a small pond that was also entirely ice covered during the sampling period. The mats in the pond were orange and crusty with many large green nostoc sheets. Small snow accumulations were present in the catchment.

Miers Valley pond descriptions

Canary

Canary pond was a small oval shaped pond that sits on the slopes to the South of the Miers Valley (Fig. 5.8 a). During sampling, the pond had no ice cover, and the water was green and cloudy. The microbial mat in the pond had two main structures. An orange microbial mat that was up to 2 cm thick, and bleached white in some sections, covered 40 % of the visible pond floor, and was evident on the non-visbile pond floor due to floating lift off mats near the pond cente. The remaining 60% of the visible pond floor was covered in an approximately 2 mm thick grey green mat with a crumbly texture. A margin of soil salts approximately 1 m wide surrounded the pond. Canary pond was 9 m long by 7 m wide and 1.05 m deep.

Macaw

Macaw pond was a semicircular pond that sits at the base of a steep catchment on the slopes of the South side of the Miers Valley mouth (Fig. 5.8 b). Except for a 30 cm margin with little mat development, the pond floor is covered by microbial mats, the dominant structure being a thick orange mat. The mat had vertical peaks and towers, and a cross section of the mat revealed pink and green layers below the orange surface. Many sections of lift off mats surround a deep pool at the northern side of the pond, which contains murky green water. The pond was 12 m long by 8 m wide. Depth could not be measured accurately, but was estimated to be 1.5 m. There was a soil salt margin with a maximum extent 2 m from the pond edge.

Robin

Robin pond was a small round pond that sits at the top of an apparent cascade of ponds within the same overall catchment (Fig. 5.8 c). Robin pond was 13 m east of Finch pond (below) and at a slightly higher elevation. There is no obvious connection between the two ponds. Two more ponds occured at lower elevation than Finch; ‘Sparrow’ pond which had a similar conductivity to Finch, and Stork pond which was a large, permanently ice-covered pond at the base of the catchment. Robin pond had a thin film of ice covering 75 % of the pond surface. The pond water was clear and colourless, and an ice plug sat at the base of the pond, covering 10 % of the pond

a)

d)

b)

e)

c)

f)

Fig. 5.8 Miers Valley study ponds in January 2013, images a - c courtesy of Clau Lizieri

a) Canary pond
b) Macaw pond
c) Robin pond
d) Finch pond
e) Kingfisher pond
f) Morepork pond

floor area. The floor of the pond in the thawed section had several mat structures. The pond edge had little mat development (10% area), and the middle depths were covered by a thick, lumpy dark green mat that appeared to be nostoc (60%). The deeper section of the pond was covered by a thick orange mat (20%). The pond is 6 m by 6 m, and the ice plug was 1.2 m deep. A soil salt margin surrounds the pond.

Finch

Finch pond was an irregularly shaped pond that is part of the 'cascading' ponds mentioned above (Fig. 5.8 d). The pond water was colourless and very clear. Cohesive microbial mats covered the pond floor. The mats at the pond edge were brown, with thicker orange mats near the deeper sections of the pond. The pond was shallow, with 3 deeper sections of approximately 40 cm depth. The pond was 10 m long and 5 m wide, and was rimmed by a 50 cm wide soil salt margin, which started 50 cm from the pond edge.

Kingfisher

Kingfisher pond was a round pond that sat beneath a 2.5 m high ice bank to the ponds north, cut into the ground ice which underlies the moraines in the area (Fig. 5.8 e). The water was very turbid, and murky brown in colour, which appears due to glacial flour contributed from the ice bank. The pond floor was visible to 20 cm depth, and the mats in this region were orange brown and 2-5 mm thick. Kingfisher pond appears to be part of a drainage system, and a small stream flowed into the western side of the pond, and out of the eastern side. The pond had 90 % thin ice cover, which was several millimeters thick. A soil salt magin 2 m wide surrounded the pond, which appeared to be mirabilite. Within the catchment, beyond the 'mirabilite' margin to the north of the pond, rocks in the soil had a white mineral coating. Depth could not be accurately measured, and is estimated at 0.5 m from the catchment characteristics and slopes.

Morepork

Morepork pond occurred on the floor of the Miers Valley, within several hundred meters of the valley mouth and Koetlittz Glacier (Fig. 5.8 f). It was comprised or two circular lobes, that were joined by an area approximately 20 cm deep in the middle. The pond floor was entirely covered by microbial mats. The pond edge had a thin grey-brown mat that was difficult to distinguish

from sediment by sight alone, but was cohesive when touched. At 5 cm depth, green and orange mats were the dominant feature, with many associated green ball structures which were cyanobacterial assemblages that sat on the mat surface. Thick orange lift off mats were dominant in the centre, and surrounded murky green water at the base of the pools. Each lobe was 1.2 m deep, and 8 m wide. The major axis of the pond was 20 m long. Some soil salts surrounded the pond, and sections of moss were also present in the catchment within several meters of the pond edge.

Ross Island Ponds

Hut Point Peninsula

OHP

OHP was a round pond located on the southern side of Observation Hill (Fig. 5.9 a). It had very clear water at the time of sampling, with bright orange mats that were not cohesive on the pond floor. There was 20 % ice cover on the pond, and half of the pond was surrounded by a large snow bank which covered much of the catchment. Some soil salts were observed near the pond edge.

a) b)

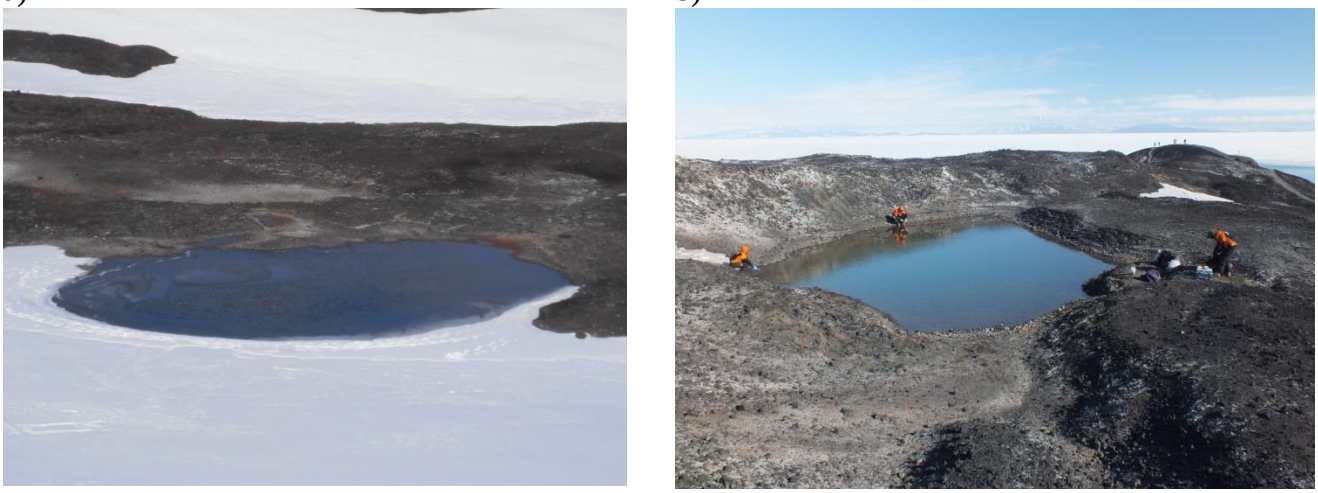


Fig. 5.9 Hut point peninsula study ponds in January 2012
a) Observation Hill Pond
b) Hut Point Pond 2, image courtesy of Ian Hawes.

HP2

HP2 was a square shaped pond near Scott's Hut at Hut Point (Fig. 5.9 b). The water was turbid, and brown-orange cohesive mats covered the visible parts of the pond floor. Red sections on the mats were due to the presence of many rotifers which were observed under a microscope. Some surface sediments from the pond had a distinctive sulfide smell, and were dark black and grey. A small snow bank was present at the ponds edge, and there was no ice cover. Soils in the catchment had a patchy distribution of soil salts.

Cape Royds ponds

Shackleton

Shackleton pond was a long narrow pond, 85 m in length, 20 m wide at the centre, and an estimated 1.2 m in depth (Fig. 5.10 a). The water was colourless and very clear. Several snow banks were located around the pond edged, and appeared to be the major meltwater source. Bright orange microbial mats covered 90 % of the pond floor. The mats had a green bottom layer, and were 1-2 cm thick. The substrate comprised black-grey soils, with black boulders. The ponds catchment had 10 – 15 % snow cover at the time of sampling.

Ernest

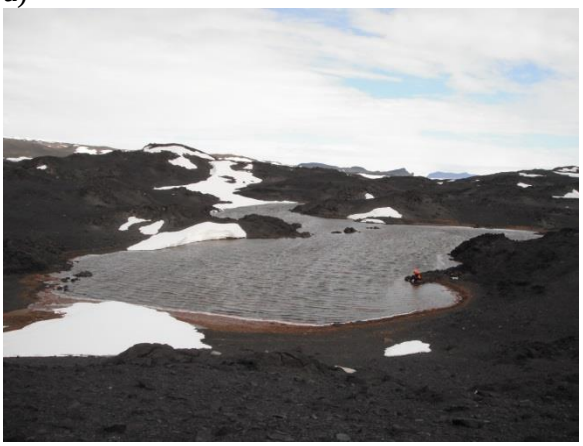
Ernest pond was an elliptical shaped pond 22 m long by 9 m wide, and an estimated 1 m deep (Fig. 5.10 b). The pond was approximately 50 m from Shackleton pond, and at a similar elevation. The pond floor was 90 % covered by orange and green microbial mats, with some bleached areas that were yellow and white. Most of the mat was a 1-2 cm thick cohesive sheet, with a flakier texture near the shore. There were dried mats around the pond edge. An area of the catchment north east of the pond had some moss and lichen growing on rocks near the pond edge. The pond had a small snowbank.

Bart

Bart pond was a shallow, elliptical shaped pond 17 m long by 10 m wide, and 50 cm deep (Fig. 5.10 c). The pond floor was covered in thin brown-orange mats that look sediment like in places.

At the time of sampling some overnight snowfall had left patchy snow cover near the pond of 1-5 cm thickness, however an established snow bank also existed to the south east of the pond.

a)



b)

c)

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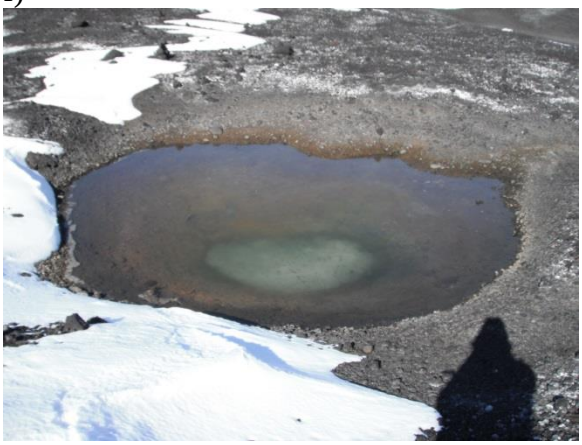


Fig. 5.10 Cape Royds study ponds in January 2011.
a) Shackleton pond
b) Ernest pond
c) Bart pond
d) Green lake
e) Penguins by Green lake
f) Nimrod Pond

Green

Green Lake was a large pond that was documented in the work of the scientists on the Nimrod Expedition in 1912 (Fig. 5.10 d). The pond consisted of 2 joined lobes, one 70 m long by 35 m wide, and one 16 m in diameter. The pond was estimated to be >1 m deep. The pond water was green in colour. Three snow banks lay on the northern, and northeastern banks. The pond floor appeared entirely covered by orange mats of 2 cm thickness, with some lift off mats. The surrounding soils were predominantly gravel, with some areas of a finer, sandy soil. Many skua were nesting near the pond, adélie penguins were frequently observed in the catchment during the sampling period, and both skua and penguins were observed in the pond water (Fig. 5.10 e).

Nimrod

Nimrod pond is a small 6 m by 7 m pond approximately 1 m deep (Fig. 5.10 f). The deepest section of the pond has an ice plug which was 1.5 by 2 m, and pale green in colour. The water was very clear, and the pond floor was covered in mats that were brown closest to the pond edge, a light brown region in the middle depths, and an orange-red colour near the centre. A thick crust of soil salts was present 40 cm above the pond level, and dried mats above the pond suggested a drop in pond level. A small snowbank was present in the catchment.

Cape Evans

Pond 2

Pond 2 was a shallow elliptical pond with clear water and 40 % ice cover. Cohesive orange mats covered the pond floor. There was a small snow bank next to the pond.

Pond 3

Pond 3 was a small pond approximately 10 m north west of pond 2. Pond 3 also had 40 % ice cover, clear water and a snow bank. The microbial mats were bright orange and cohesive.

Pond 9

Pond 9 was a small irregularly shaped pond. There was a snow bank at the side of the pond, and the pond had 50 % ice cover. Orange-brown mats covered the pond floor.

Table 5.1 Physical characteristics of pond reservoirs. * Denotes an elevation estimated using Google Earth, used in absence of one measured on a GPS. Google Earth elevation estimates were accurate to within ± 100 m for the other sampling areas, and were typically lower than the measured elevation.

Pond	Length (m)	Breadth (m)	Depth (m)	% Ice cover (thickness, cm)	Elevation (m)	Latitude (E)	Longitude (S)
Lower Wright Valley							
LW2	30	20	0.6	0	250	162 41 30.3	77 26 43.9
LW7	17	8	-	0	295	162 42 46.0	77 26 41.6
LW12	24	22	1	0	294	162 39 00.5	77 27 00.1
LW13	20	8	1	95 (0.5)	283	162 38 52.5	77 27 02.0
LW14	16	7	0.4	50 (0.5)	291	162 38 44.7	77 27 02.8
LW15	15	12	0.5	90 (0.6)	289	162 38 35.3	77 27 03.1
LW16	20	15	0.8	100 (9)	289	162 38 28.6	77 27 03.0
LW18	10	10	0.6	100 (6)	291	162 38 19.3	77 27 02.7
Miers Valley Mouth							
Canary	9	7	1.05	0	61*	164 11.453	78 07.433
Macaw	12	8	1.5	0	36*	164 12.243	78 07.619
Robin	6	6	1.2	90 (0.5)	52*	164 11.762	78 07.752
Finch	8	6	0.4	0	52*	164 11.714	78 07.748
Kingfisher	10	8	0.5	0	86*	164 10.416	78 07.754
Morepork	20	8	1.23	0	55*	164 12.061	78 07.343
McMurdo Station							
OHP	30	20	0.3	20	60	166 41 25.7	77 51 20.9
HP2	16	8	1	0	28	166 38 36.8	77 50 41.8
Cape Royds							
Shackleton	85	25	1.5	0	73	166 09 55.6	77 32 19.6
Ernest	22	9	1	0	73	166 10 01.8	77 32 16.9
Bart	17	10	0.5	0	<100	166 69 52.3	77 32 57.5
Green Lake	70	40	1	0	66	166 08 57.9	77 32 31.9
Nimrod	7	6	1.75	0	30	166 10 37.1	77 32 56.5
Cape Evans							
Pond 2	18	10	0.35	45 (0.5)	10	166 24 35.2	77 38 21.2
Pond 3	18	9	0.5	0	15	166 25 30.3	77 38 11.6
Pond 9	24	12	0.45	20 (0.3)	11	166 25 38.2	77 38 11.4

5.3 Results

5.3.1 Pond structure and reservoir volumes

The study ponds ranged in length from 6 m to 85 m (Table 5,1). The visible pond floors continued subaerial ground relief, and appeared similar to the conical shaped ponds for which detailed bathymetry was measured at Bratina Island. Lateral soil profiles were measured at Macaw and Canary ponds in the Miers Valley (Fig. 5.11). Ice cemented ground (permafrost) was found at depths of 25 – 57 cm below the soil surface throughout the Miers Valley sampling area, and the average permafrost depth was 41 cm. A hole dug at Canary pond revealed a glassy ice surface at the soil – permafrost interface. Depth to ice cement beneath sediments was also measured at Canary, Finch and Robin ponds, and ranged from 39 – 65 cm. Permafrost depth was not measured in the Lower Wright Valley or Ross Island.

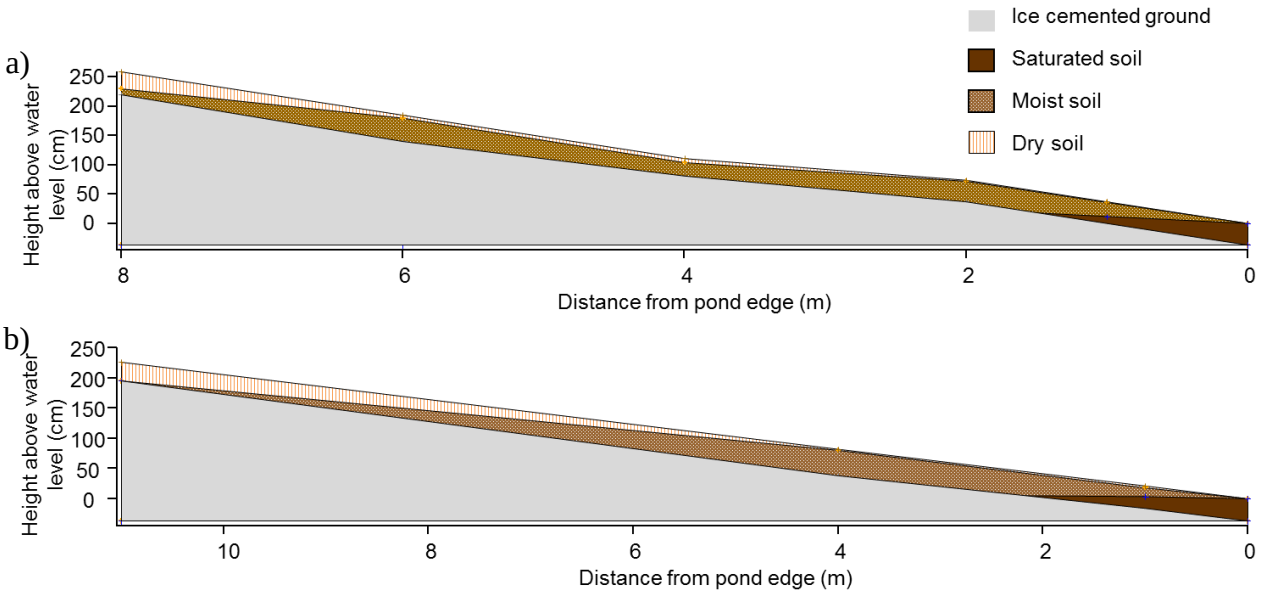


Fig. 5.11 Cross sections displaying the soil and water table structure measured at 1 to 3 m intervals on transects to the east of two selected Miers Valley ponds

c) Canary pond
d) Macaw pond

Surface soils surrounding the ponds were moist in a 1-3 m wide margin around the pond edge. At the edge of this moist zone, many ponds had a rim or patches of soil salts present. The soil profiles at the Miers Valley ponds revealed that saturated soil persisted under the soil surface in a water table structure around the ponds. This extended horizontally approximately 2 from the pond edge on the eastern sides of Canary and Macaw ponds, and vertically by an estimated 10 – 20 cm (Fig. 5.11).

The model of pond structure outlined in Chapter 2 was applied to the ponds to calculate the pond reservoir volumes (Table 5.2). Shackleton pond and Green Lake were the largest ponds, and had the largest reservoir volumes. Robin pond was the smallest pond, and correspondingly had the smallest reservoir volumes.

Table 5.2 Calculated pond reservoir volumes.

	Water volume (m^3)	**Mat volume (m^3)**	**Sediment volume (m^3)**	**Saturated soil volume (m^3)**
Lower Wright Valley				
LW2	98	0.5	221	31
LW12	138	0.4	188	29
LW13	51	0.2	70	20
LW14	14	0.1	47	17
LW15	24	0.2	65	19
LW16	64	0.3	109	23
LW18	16	0.09	36	16
Miers Valley Mouth				
Canary	18	0.06	23	14
Macaw	39	0.1	37	16
Morepork	63	0.2	70	20
McMurdo Station				
HP2	38	0.3	52	18

5.3.2 Pond reservoir chemistry

Water reservoir

The ponds ranged in conductivity from 0.23 – 56.2 mS/cm (Table 5.3). At both the Lower Wright Valley and Ross Island, a broad range of conductivities was observed (from < 1 to > 28 mS/cm). Surface conductivities had a lower range at the Miers Valley (0.63 – 4.29 mS/cm), however all of the Miers Valley ponds (except for Kingfisher, where stratification was not observed) were chemically stratified, with basal conductivites ranging from 2.82 – 103.9 mS/cm. The pH of all of the study ponds was alkaline, ranging from 8.05 at LW2 in the Lower Wright Valley, up to 10.41 in Pond 3 at Cape Evans. The pH range in the Lower Wright Valley ponds was lower than the other two sample sites. Dissolved oxygen concentrations ranged from 11.7 – 16.18 mg/L. The ponds in the Lower Wright Valley had the lowest range of DO concentrations, and those at Cape Evans on Ross Island had the highest.

Table 5.3 Pond water chemical characteristics. The pH, DO and conductivity values are the average of 3 readings, other data is from a single sample. Values with * are from unpublished data collected from these same ponds in 2010 by Ian Hawes and Jenny Webster-Brown. na represents a value was not analysed, and – represents a value that could not be calculated.

Pond	Conductivity (mS/cm)	pH	DO (mg/L)	DRP (µg/L)	DOP (µg/L)	PP (µg/L)	TP (µg/L)	TIN (µg/L)	DIN:DRP (mole ratio)
Lower Wright Valley									
LW2	28.17	8.05	12.28	<1	4	5.2	9.2	75620	330000
LW7	0.84	8.41	11.70	64	15	24	103	1808	62
LW12	14.45	8.11	12.43	<1	11	9.4	20.4	17436	77000
LW13	9.02	8.77	13.95	<1	4	10.3	14.3	74108	330000
LW14	5.39	8.33	13.44	6	6	48.5	60.5	3056	1100
LW15	2.74	8.37	12.70	2	3	11.2	16.2	1635	1600
LW16	0.23	9.69	13.35	<1	2	6.3	8.3	863	3800
LW18	0.25	9.93	12.00	<1	3	5.3	8.3	39	170
Miers Valley Mouth									
Canary	4.29	9.51	15.70	59	56	64	179	19*	0.71
Macaw	5.80	9.96	14.63	16	8	31	55	53*	7.3
Robin	0.63	10.06	13.94	3	64	9	76	55*	41
Finch	1.74	9.76	13.35	4	68	27	99	15*	8.3
Kingfisher	0.99	9.39	14.02	5	5	43	53	7*	3.1
Morepork	4.07	8.80	12.86	<2	153	na	153	na	-
McMurdo Station									
OHP	0.54	9.81	14.22	9	30	61.5	100.5	11	2.9
HP2	1779.67	9.69	14.01	32	24	44.3	100.3	6	0.45
Cape Royds									
Shackleton	1.12	9.69	13.97	2	66	12	80	10	11
Ernest	2.42	9.56	14.05	2	16	15	33	71	79
Bart	56.20	9.23	12.99	3	32	19	54	31	23
Green Lake	4.31	10.24	14.46	102	82	166,000	166184	119	2.6
Nimrod	7.24	8.96	13.88	33	12	37	82	9	0.60
Cape Evans									
Pond 2	5.84	10.09	16.18	71	31	63	165	7	0.23
Pond 3	9.76	10.41	16.02	16	26	56	98	12	1.7
Pond 9	7.41	9.06	14.10	29	43	95	167	14	1.1

Table 5.4 Major ion chemistry of pond waters analysed by HPIC.

Pond	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)
Lower Wright Valley								
LW2	14500	2390	165	67.4	6740	806	1630	664
LW7	216	141	250	7.69	121	15.5	32.7	72.8
LW12	6380	1950	90.4	311	3020	412	754	614
LW13	4330	229	62.6	304	1790	177	544	151
LW14	2200	805	110	12.4	1060	126	231	228
LW15	1070	315	78.8	7.06	518	62.8	110	94.6
LW16	84.4	28.5	9.28	2.81	47.0	4.65	12.0	16.3
LW18	64.3	35.4	2.90	0.05	46.8	3.09	5.54	12.7
Miers Valley Mouth								
Canary	780	611	142	0.95	869	28.3	25.7	27.5
Macaw	1540	386	90.5	0.03	1110	56.3	47.7	47.1
Robin	127	39.1	50.9	0.03	123	6.19	3.03	4.33
Finch	415	123	88.5	0.03	314	21.4	21.3	25.5
Kingfisher	148	140	124	1.35	179	10.0	11.4	14.3
Morepork	1040	263	na	<dl	1080	66.0	153	155
McMurdo Station								
OHP	505	410	288	0.2	486	15.1	34.6	17.6
HP2	174	31.6	181	0.2	116	10.8	14.5	14.7
Cape Royds								
Shackleton	282	32.1	4.31	<dl	153	31	16.8	11.9
Ernest	647	88.4	8.16	<dl	310	69	40	54
Bart	21000	1890	27.5	<dl	11500	1880	1320	200
Green Lake	1100	144	4.16	<dl	750	101	69	20
Nimrod	2420	346	7.06	<dl	1320	105	152	40
Cape Evans								
Pond 2	2230	117	5.18	<dl	1350	89	170	42
Pond 3	3170	400	3.61	<dl	1830	103	250	98
Pond 9	1020	224	3.06	<dl	1090	43	130	52

Major ion chemistry was typically dominated by Na^+ and Cl^- (Table 5.4). The coastal ponds at Ross Island showed ionic compositions most similar to seawater. Ponds at Cape Royds and Cape Evans had major ion compositions very similar to standard seawater (Millero *et al.* 2008), with some Cape Royds ponds displaying HCO_3^- and Ca^{2+} enrichment relative to seawater. Of the ponds at Hut Point Peninsula, OHP had HCO_3^- and Ca^{2+} enrichment, but other element ratios were similar to seawater. HP2 showed some Na^+ and SO_4^{2-} enrichment relative to seawater. Ponds at Bratina Island and the Miers Valley had similar Mg to Ca ratios of approximately 1.5, with varying degrees of $Na^+ + K^+$ dominance. In contrast, the Lower Wright Valley and the

Upper Wright Valley had similar $Na^+ + K^+$ to Mg^{2+} ratios of approximately 2 and 5 respectively, with varying Ca^{2+} concentrations. Anion compositions were more variable within sites than cation compositions. Many ponds from several sampling areas had $Cl^-:SO_4^{2-}$ ratios of approximately 10, with varying HCO_3^- concentrations. One or more ponds at the McMurdo Ice Shelf, Miers Valley, and both sites in the Upper Wright Valley had $Cl^-:SO_4^{2-}$ ratios of 5 or less.

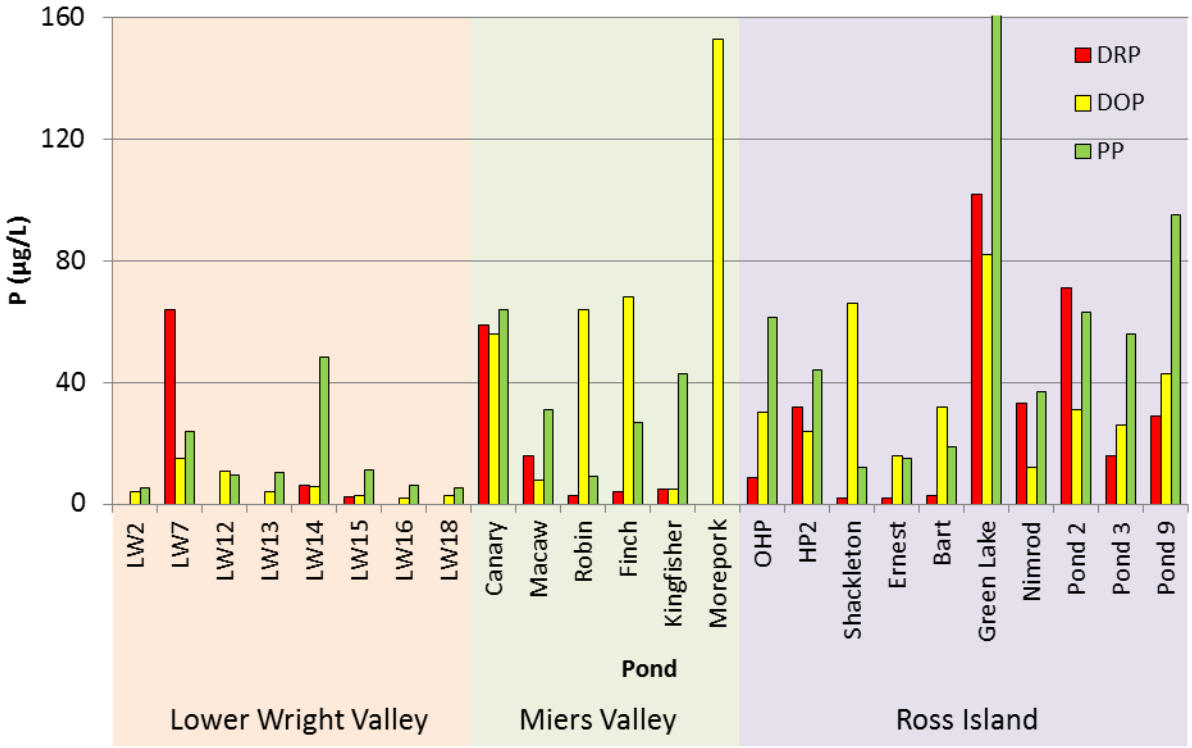


Fig. 5.14 Water column P concentration and speciation in ponds at each sample site. Where bars are not present the P concentration was below the detection limit of 1 µg/L, except for at Morepork pond where the PP filter was contaminated, so no value is shown. The Green Lake PP concentration was abnormally high and is truncated in this graph.

Total P concentrations ranged from 8.3 – 179 µg/L (excluding Green Lake), and were generally lowest at the Lower Wright Valley ponds, while Miers Valley and Ross Island ponds had broadly similar concentrations. The water column P composition was generally dominated by particulate P, however there were also instances of DOP and DRP being the dominant P form in ponds. DOP concentrations were typically higher than DRP concentrations. Green Lake at Cape Royds had an abnormally high PP value of 166,000 µg/L. Comparison of PP:PN:PC ratios at Green Lake and the other ponds at Cape Royds reflected an unusual excess of PP.

Nutrient concentrations ranged from below detection to more than 100 µg/L DRP, and more than 75000 µg/L NO_3-N. DRP concentrations were typically lowest in the Lower Wright Valley, with the exception being LW7 pond (which had a notably high concentration of 64 µg/L DRP). The Lower Wright Valley also had the highest dissolved inorganic N concentrations, and resulting DIN:DRP ratios of 28 or greater. The Miers Valley ponds had DRP concentrations ranging from below detection to 59 µg/L. NO_3-N was not analysed for the 2013 samples, however analyses performed on samples from the same ponds in 2010 reveal NO_3-N concentrations of 4-48 µg/L, and DIN:DRP ratios of 0.4-5 (calculated from 2010 DIN and DRP data). On Ross Island the range of DRP concentrations was 2 – 102 µg/L, and both extremes were measured in samples from Cape Royds. Ernest and Shackleton ponds had the lowest DRP values, and the highest value was measured in Green Lake. Ranges at Hut Point Peninsula and Cape Evans were narrower, 9-32 and 16-71 µg/L respectively. NO3-N concentrations at Hut Point Peninsula and Cape Evans ranged from below detection to 1 µg/L. In contrast, those measured at Cape Royds ranged from 1-90 µg/L, and were also highest in Green Lake. Ratios of DIN:DRP were typically less than 3 on Ross Island, and always less than the Redfield ratio of 16:1, with the exception of Ernest and Bart ponds at Cape Royds, which had ratios of 79:1 and 23:1 respectively.

The pond water was the smallest reservoir of P in all of the ponds studied, and was generally ≤ one order of magnitude smaller than the mat reservoir (Table 5.5). The main exceptions were Shackleton, Nimrod and Green Lake at Cape Royds, where the water column had closer to half of the P content of the mat, and may be considered similar due to the 50 % error estimated in the reservoir content calculations.

Mat reservoir

The ponds floors were generally entirely covered by microbial mats. The mats varied in colour and appearance, within and between ponds and sample sites. At the Miers Valley for instance, some ponds appeared to have several different mat morphologies within the same pond. Descriptions of mats are given in the pond descriptions in section 5.2.2 of this chapter.

Biomass of the mats ranged from 0.30 to 2.86 kg/m^2 (Table 5.6). Values were typically highest in the Miers Valley ponds. The lowest values were measured at Hut Point Peninsula, however the other Ross Island sites typically had greater biomass values than the Lower Wright Valley.

Table 5.5 Calculated values of pond P reservoir content in 2013. na = not analysed, * = value has been calculated using half of the detection limit as a concentration estimate. Only the ponds that had sediment sampled are displayed, as sediment was typically the major reservoir.

	Water reservoir				Mat	Sediment reservoir						Soil reservoir		
						Whole reservoir			Top 5 cm					
	Total P (kg)	**DRP (kg)**	**DOP (kg)**	**PP (kg)**	**Total P (kg)**	**Total P (kg)**	**Reactive P (kg)**	**Apatite P (kg)**	**Total P (kg)**	**Reactive P (kg)**	**Apatite P (kg)**	**TP (kg)**	**Reactive P (kg)**	**Apatite P (kg)**
Lower Wright Valley														
LW2	0.0009	0.00005*	0.0004	0.0005	0.09	100	10	100	10	1	10	20	0.5	20
LW13	0.0007	0.00003*	0.0002	0.0005	0.1	50	4	50	6	0.5	5	20	0.3	20
LW14	0.0008	0.00008	0.00008	0.0007	0.07	30	3	30	4	0.3	3	20	0.4	20
LW15	0.0004	0.00005	0.00007	0.0003	0.1	40	4	30	4	0.4	4	20	0.6	20
LW16	0.0005	0.00003*	0.0001	0.0004	0.05	70	7	60	8	0.8	7	20	0.5	20
LW18	0.0001	0.000008*	0.00005	0.00008	0.06	20	2	20	2	0.3	2	10	0.1	10
Miers Valley Mouth														
Canary	0.003	0.001	0.001	0.001	0.06	40	1	30	4	0.1	4	50	1	50
Macaw	0.002	0.0006	0.0003	0.001	0.09	70	3	70	8	0.3	7	60	1	60
Morepork	0.01	0.00003	0.01	na	0.3	100	3	100	10	0.4	10	na	na	na
McMurdo Station														
HP2	0.003	0.0009	0.002	0.0002	0.05	200	5	200	20	0.5	20	40	2	10

Mass loss on ignition values ranged from 6.88 – 49.22 %, lowest at the Lower Wright Valley and highest at Hut Point Peninsula. The P content of the mat did not show a strong spatial pattern, concentrations below 500 mg/kg were measured at LW2 and LW16 ponds in the Lower Wright Valley, and at Bart Pond at Cape Royds (Fig. 5.15 a). The other ponds typically had mat P concentrations of 1000-2000 mg/kg. Average concentrations at each area reveal lower mat P is typical at the Lower Wright Valley, and the highest at Ross Island. The samples from Cape Royds and Cape Evans were treated differently than those from the other areas, P content is estimated from N and C content values, and LOI was not measured. There was a general trend of increasing average P content with increasing average LOI across all sample sites, with the exception of Bratina Island which had uniformly low LOI with varying P content (Fig. 5.15 b). The average biomass did not correlate strongly with average P content (Fig. 5.15c).

The mat was the second smallest reservoir of P in the ponds, and contained from 50 g, to 300 g of P in the main ponds (Table 5.5). Other study ponds for which incomplete sampling of the reservoirs was performed contained up to 2 kg of P (Appendix 1). No correlation was observed between mat volume and P concentration.

Sediment reservoir

Sediments were typically sandy in texture, and varied in colour between the sites. The soils in the Lower Wright and Miers Valley were generally grey, however some ponds had a black, sulfide smelling layer of several centimetres thickness below the microbial mat. The sediments at Hut Point Peninsula were black in colour, and no sulfide smell was observed. Psenner extractable P content ranged from 248 mg/kg P at LW2 pond in the Lower Wright Valley, to 1973 mg/kg P in HP2 at Hut Point Peninsula. Total Psenner extractable P concentrations were lowest in the Lower Wright Valley ranging from 248 – 375 mg/kg, and more than double this at the Miers Valley (767 – 947 mg/kg). At all ponds, sediment was the major reservoir of P, the only exception was at Canary pond in the Miers Valley, where the saturated soil was the major reservoir. The P content of the sediments ranged from 20 to 200 kg, comprising 44 to 83 % of pond P.

Sediment P was predominantly in the form of apatite P (88 to 98 %) in all of the study ponds. Reactive P fractions comprise the remaining 2 to 12 %, of which metal oxide adsorbed and organic P (MO-P) or reducible oxide adsorbed P (RO-P) was the dominant fraction (Fig. 5.16).

Ponds of the Lower Wright Valley had the highest proportion of reactive P (8-12 %). Sediment cores were taken at LW15, LW18, Canary, Macaw, Morepork and HP2 ponds, and had P concentrations similar to bulk sediment samples where these were taken. No coherent trend was seen in the concentration of P fractions with depth in the sediment cores at any of the ponds.

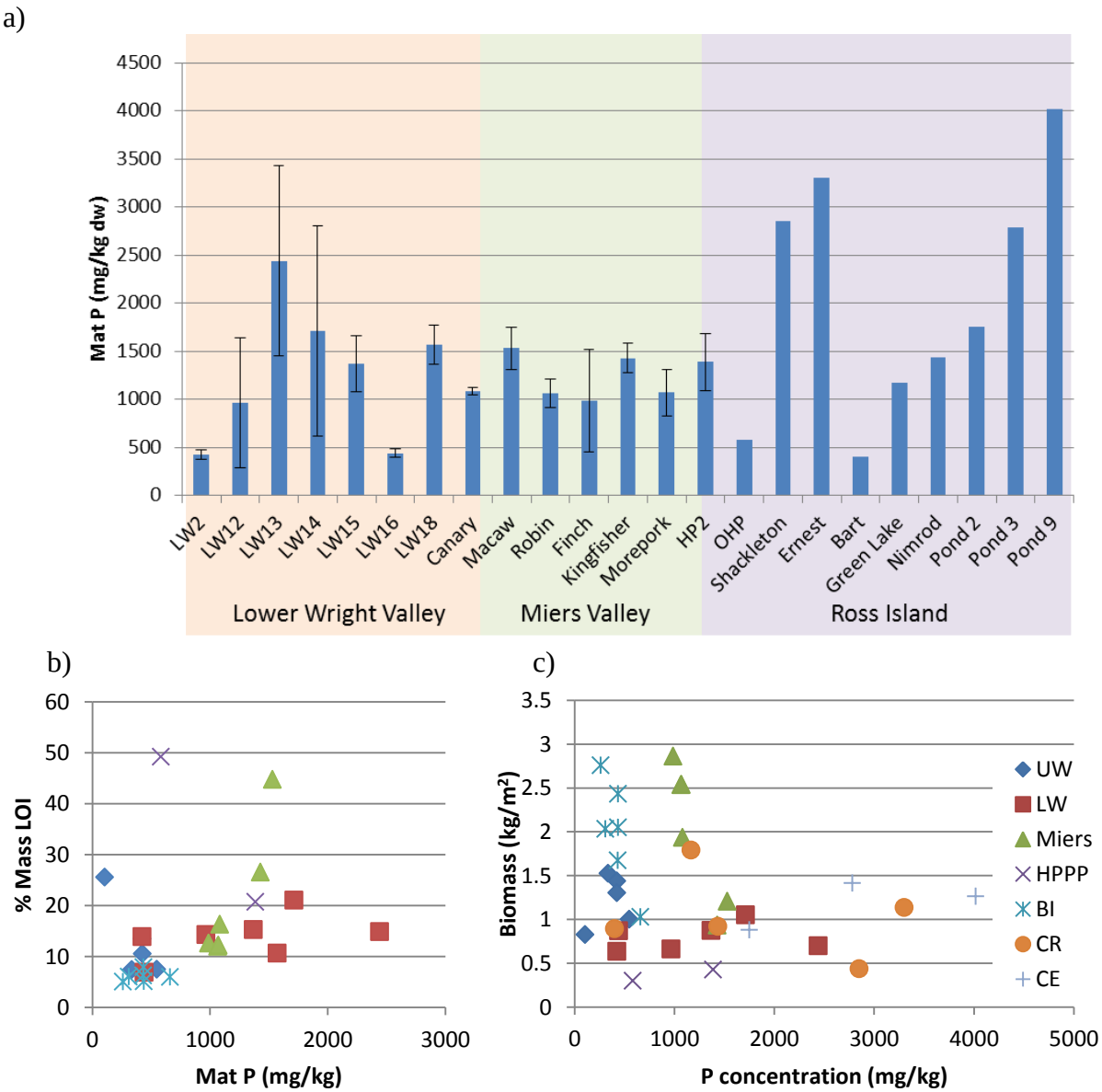


Fig. 5.15 Microbial mat P, mass LOI and biomass data at each sample site (including Bratina Island and Upper Wright Valley).

a) Average P concentration in pond microbial mats, and the standard deviation of the 5 samples analysed (error bars). Cape Royds and Cape Evans results derived from ratio to N and C.
b) The average percent mass loss on ignition plotted against average mat P concentration.
c) The average mat biomass plotted agains average P concentration in each pond.

Table 5.6 Pond microbial and substrate chemical characteristics in 2013. Data is from a single sample unless an n value is specified, in which case an average is given. Values with * have been calculated from nitrogen and carbon concentrations, using ratios established by Hawes (2011). na = not analysed.

	Mirobial mat (n=5)			Sediment			Soil		
Pond	**Biomass (kg/m2)**	**P (mg/kg)**	**Mass LOI**	**Total P (mg/kg)**	**Reactive P (mg/kg)**	**Apatite P (mg/kg)**	**Total P (mg/kg)**	**Soluble P (mg/kg)**	**Apatite P (mg/kg)**
Lower Wright Valley									
LW2	0.89	423	13.9	248	28.5	219	402	1.41	393
LW12	0.64	965	14.28	na	na	na	401	0.83	396
LW13	0.66	2440	14.85	375	31.1	342	400	2.12	392
LW14	0.7	1710	21.06	342	32.3	309	510	0.35	498
LW15	1.05	1370	15.29	291	30.1	261	566	1.89	551
LW16	0.87	440	6.88	312	31.2	281	495	1.48	484
LW18	0.87	1570	10.66	271	32.7	239	418	0.41	414
Miers Valley									
Canary	1.93	1080	16.31	767	26.4	741	1653	7.69	1615
Macaw	1.21	1530	44.78	947	40.9	906	1785	5.57	1745
Morepork	2.54	1070	12.19	922	23.4	899	na	na	na
Hut Point Peninsula									
HP2	0.30	1386	49.22	1973	44.5	1929	1231	10.9	1180
Cape Royds									
Shackleton	0.44	2850*	na	na	na	na	1458	8.8	1410
Bart	0.89	400*	na	na	na	na	1380	6	1350
Nimrod	0.92	1430*	na	na	na	na	1348	8.7	1300
Cape Evans									
Pond 2	0.88	1750*	na	na	na	na	1287	12.1	1240

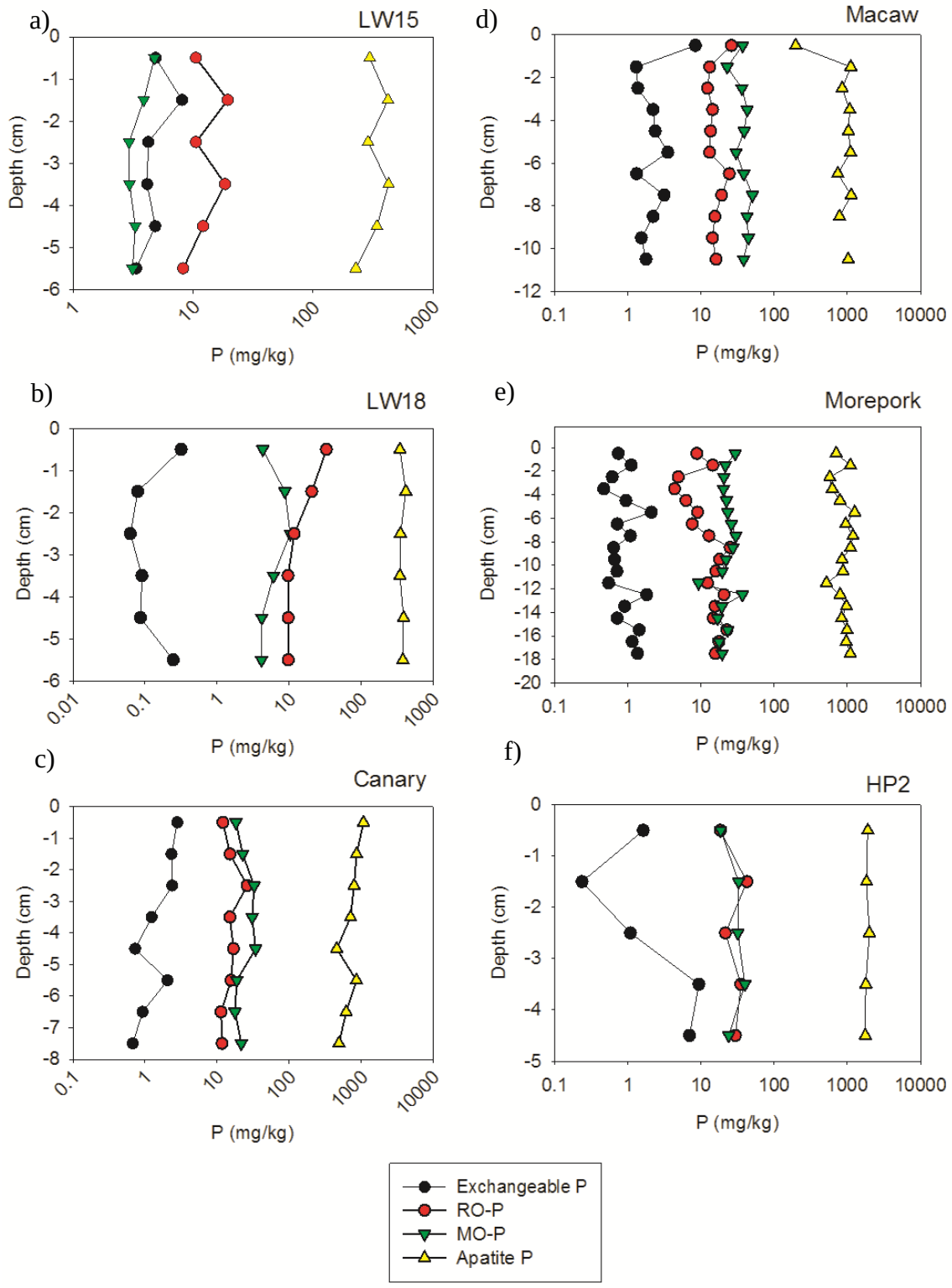


Fig. 5.16 Sediment Psenner fractionation data for cores collected from
a) LW15 pond
b) LW18 pond
c) Canary pond
d) Macaw pond
e) Morepork Pond
f) HP2

At most ponds, the top 1 cm of the core, which contained the microbial mat and underlying sediment, had higher exchangeable P concentrations relative to the sediment at 1-2 cm depth. However, this was not observed at LW15 and Morepork ponds, where the surface sample had less exchangeable P. LW18 pond had the lowest measured exchangeable P concentrations in the sediment core (ranging from 0.06 – 0.32 mg/kg), while LW15 pond had the highest exchangeable P concentrations (3.3 – 8.1 mg/kg), and was the only pond where the exchangeable P fraction was larger than the MO-P fraction. Interestingly, these ponds also showed opposite patterns in exchangeable P concentrations. The surface and deepest (5-6 cm depth) parts of the LW18 core had the highest exchangeable P concentrations, while the lowest exchangeable P concentrations at LW15 pond was at the base of the core. Below the enriched surface sample, exchangeable P at HP2 increased with depth. The exchangeable P concentrations at the Miers ponds varied with depth by a factor of up to 4, but no trend was evident.

The ponds from the Lower Wright Valley had higher concentrations of RO-P than MO-P, in contrast to the Hut Point Peninsula and Miers Valley ponds which had higher MO-P concentrations. The concentrations of both MO-P and RO-P differed by factors of 2-4 within cores, and again no coherent trend was apparent with depth. Rather, the 2-4 fold fluctuations seemed to occur throughout the length of most of the cores. Average MO-P concentrations were lowest in the Lower Wright ponds (2.9 – 10.4 mg/kg) where RO-P concentrations were greatest (8.3 – 33 mg/kg). MO-P concentrations at HP2, Canary and Morepork ponds were similar ranging from 9.2 – 40 mg/kg, while Macaw pond had a higher range of 23 – 50 mg/kg MO-P.

Apatite P concentrations in the cores were lowest in the Lower Wright Valley (228 – 427 mg/kg), and highest at Hut Point Peninsula (1760 – 2000 mg/kg). Again, no significant correlation existed with depth, however a pattern was observed where several ponds had lower apatite P concentrations in the 0-1 cm depth sediment than the underlying sediment. This was most pronounced at Macaw pond, where the apatite P concentration increases from 197 to 1100 mg/kg between the top two slices of the sediment core. This pattern was also observed at LW15, LW18 and Morepork ponds, but was not observed at HP2 or Canary ponds.

Sediment P fractionation typically showed the lowest concentrations of the most reactive fractions, in a pattern of exchangeable P < RO-P < MO-P < apatite P. However, in the Lower Wright Valley, RO-P was present at greater concentraiton than MO-P in the ponds, as was

exchangeable P in LW15. In all ponds, 88 to 98 % of the total Psenner extractable P was in the form of apatite P.

Fig. 5.17 Hedley fractionation data from soils close to the study ponds at each site

Soil reservoir

The soils in the Lower Wright Valley and the Miers Valley were sandy, loose and grey in colour (Fig. 5.7 and 5.8). Those on Ross Island were a dark grey-black colour, and were firm with many rocks on the surface (Fig. 5.9 and 5.10). Soil salts were present at many of the ponds, in a rim or in patches surrounding the zone of moist soil at the pond edge. Salt crystals in the soils at Cape Royds and Cape Evans were identified by SEM-EDS and included halite, sodium sulfate

(mirabilite), and unidentified rectangular crystals comprised of mixed K, Na, SO_4 and Cl. No detectable P (i.e., < 1atomic %) was present in any of the analysed salt crystals.

The saturated soil reservoir of the study ponds contained 10 kg (LW18) – 200 kg (Shackleton) of total P (Table 5.5). In all ponds, saturated soil was the second largest reservoir of P in the ponds, the only exception being Canary pond where saturated soil was the largest reservoir. Saturated soils had several orders of magnitude more P than the pond water and mat.

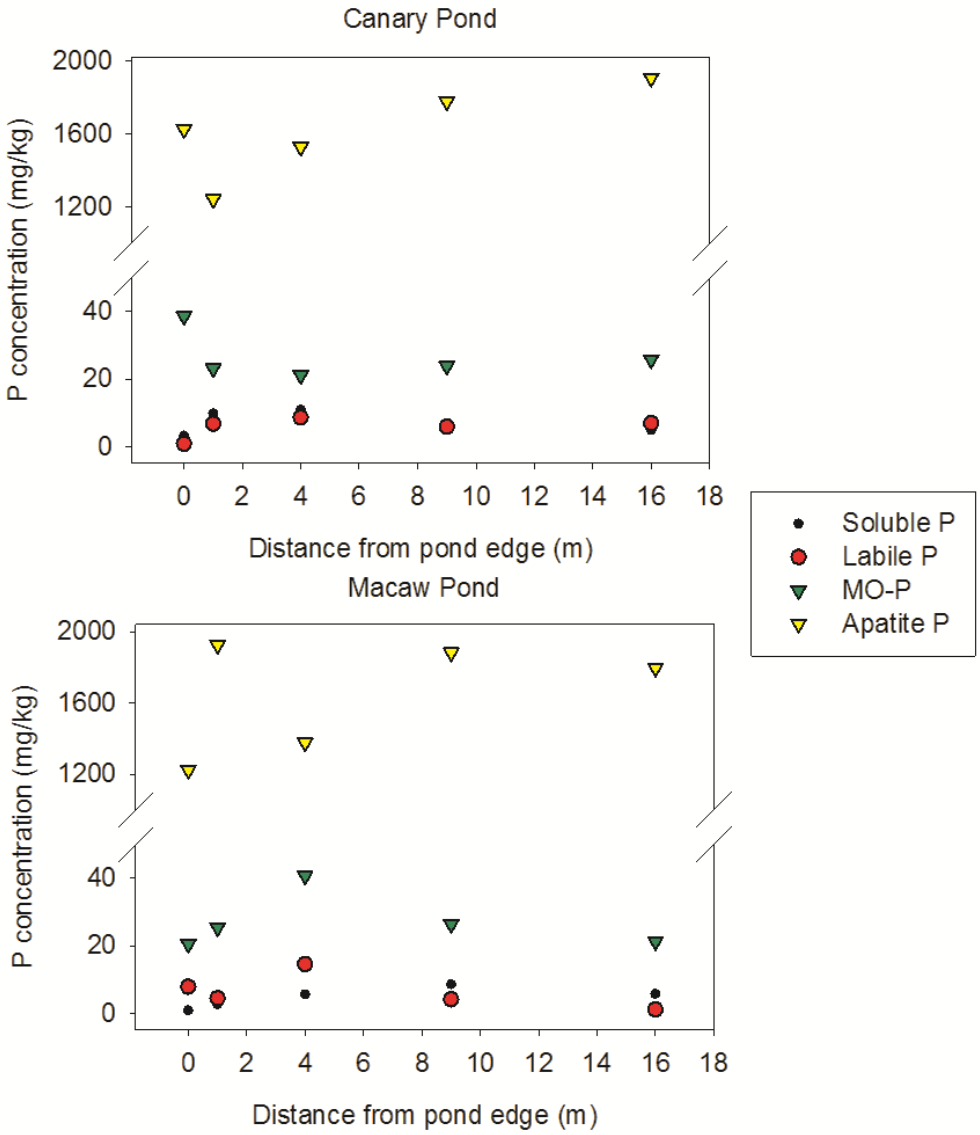


Fig. 5.19 Soil Hedley P fractionation data for transects to the north of Canary and Macaw ponds in the Miers Valley

a) Canary pond.
b) Macaw pond.

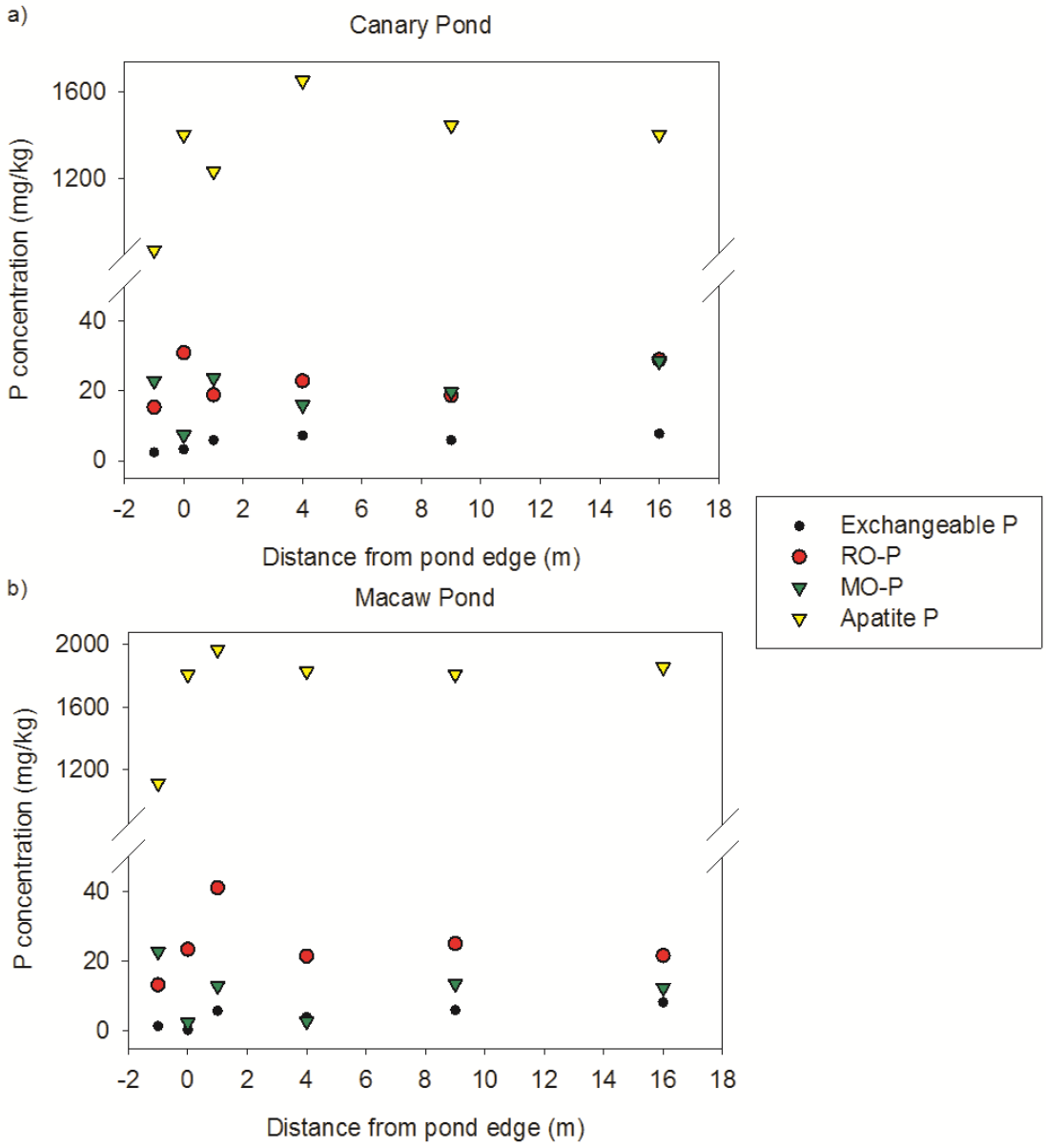


Fig. 5.19 Psenner P fractionation data for a surface sediment (brown shading) and soil samples taken along transects to the north of Canary and Macaw ponds in the Miers Valley

a) Canary pond
b) Macaw pond

Hedley extractable total P concentrations ranged from 400 mg/kg at LW13 pond to 1745 mg/kg at Macaw pond (Table 5.6). The Lower Wright Valley had the lowest soil total P concentrations (400 – 566 mg/kg), and the Miers Valley the highest (1615 – 1745 mg/kg). Values at Ross Island were intermediate, ranging from 1231 – 1458 mg/kg. The dominant form of P in soils was apatite P, which comprised 95 - 98 % of the Hedley extractable total P (Fig. 5.17). Reactive P fractions comprised the remaining 2 to 5 %. There was relatively little soluble P present in the soils – with

the lowest concentrations of 0.4 to 2.1 mg/kg measured at the Lower Wright Valley, and the highest concentrations of 8.7 – 12.1 mg/kg measured on Ross Island. Soluble P was often the minor reactive P phase in soils, particularly at Ross Island and in the Miers Valley. Labile P was not detected in the soils at 3 of the ponds at the Lower Wright Valley, but was the dominant reactive P phase at 3 other ponds in the area. MO-P tended to dominate reactive P phases at the other ponds, comprising 0.8 – 2.5 % of the total P.

Pond sediments typically contained 46 – 70 % of the total P in surrounding soils, the two exceptions were LW13 pond where concentrations were similar, and HP2 pond where sediments had substantially more P than was present in the soils (Table 5.6). Soil sampled from transects measured to the north of Canary and Macaw ponds were analysed for P fractionation, using both the Psenner and Hedley methods. The total P in sediments was less than that in soils, and the exchangeable and soluble P concentrations were lowest in the sediment and the saturated soil sampled at the pond edge (Fig. 5.16 and 5.17). Soluble P concentrations increased with distance from the pond edge within the first 5 m of the pond, and then seemed to stabilize. A similar pattern was seen in exchangeable P in the Psenner fractionation, which continued into the sediment at Canary pond, though the saturated soil at the edge of Macaw had less exchangeable P than the sediment. This pattern was mirrored in the MO-P fraction of the Psenner extraction, and was seen at both Canary and Macaw ponds where MO-P concentrations were lowest at the pond edge, and higher concentrations were found both in the sediment and in soils further from the pond. Interestingly, the Hedley analysis revealed the MO-P fraction at Canary pond, and the labile P fraction at Macaw pond were higher in the saturated soil at the pond edge than the soil moist soil at 1 m distance from the pond.

5.4 Discussion

5.4.1 P distribution in pond reservoirs

Distribution of P across pond reservoirs was similar in all of the ponds. The major reservoir of P in the study ponds at all of the sites was the sediment which held 44 – 83 % of pond P. The one exception was Canary pond, where the saturated soil held the most P (Table 5.5, Fig. 5.20). Saturated soil was the second most dominant reservoir which held 17 – 56 % of pond P, with the water column and microbial mat holding less than 1 % of pond P.

5.4.2 P speciation and availability

The study ponds displayed some key differences between the 3 sample sites. P abundance was generally highest in the water column of the coastal Ross Island ponds, and lowest in the Lower Wright Valley. The measured N:P ratios were highest in the Lower Wright Valley, and were also high in some ponds at Cape Royds.

Sediments of all ponds were dominated by apatite P, with reactive forms of P comprising less than 12 % of the total P. The reactive fractions typically comprised 10 % of the total P in Lower Wright Valley sediments, and less than 5 % of total P in the other sampling areas. This difference in composition was due to the lower total P concentrations in the Lower Wright sediments, as reactive P concentrations were broadly similar between sites, varying from 23 – 45 mg/kg.

For most ponds, the sediments contained P concentrations that were 70 % or less of the P concentrations measured in soils. This has been interpreted as an indication that sediment P is lost to the pondwater over time, and that sediments are a major P source to pond ecosystems. The one exception was sediments at HP2 on Ross Island which had much higher P concentrations (1791 – 2034 mg/kg) than any of the soils measured on Ross Island (1231 – 1458 mg/kg). This is the only study pond where sediment P was higher than soil P, and all 5 samples in the core were in this high range. This result is in contrast to the pattern seen in all other pond systems in this study. The Hut Point Peninsula has been a point of anthropogenic activity for over 100 years, and perhaps some result of human activities has introduced P to the pond sediments. This result requires further probing, and would be enhanced by XRD analysis of the soils and sediments, together with particle size analysis, and measurement of sediment P in other Ross Island ponds.

The soils are the second largest reservoir of P in the ponds, and are also dominated by apatite P. In the Miers Valley, soils had approximately double the P concentrations measured in the sediments. This difference between soil and sediment was larger than observed at the other sites, and may indicate greater pond age. If ponds have been established for a longer time in the Miers Valley, it is likely a greater proportion of P will have been weathered and transported from the sediment. As seen at Bratina Island, the difference in soil and sediment P indicates a net loss of P from ponds over time (Chapter 3).

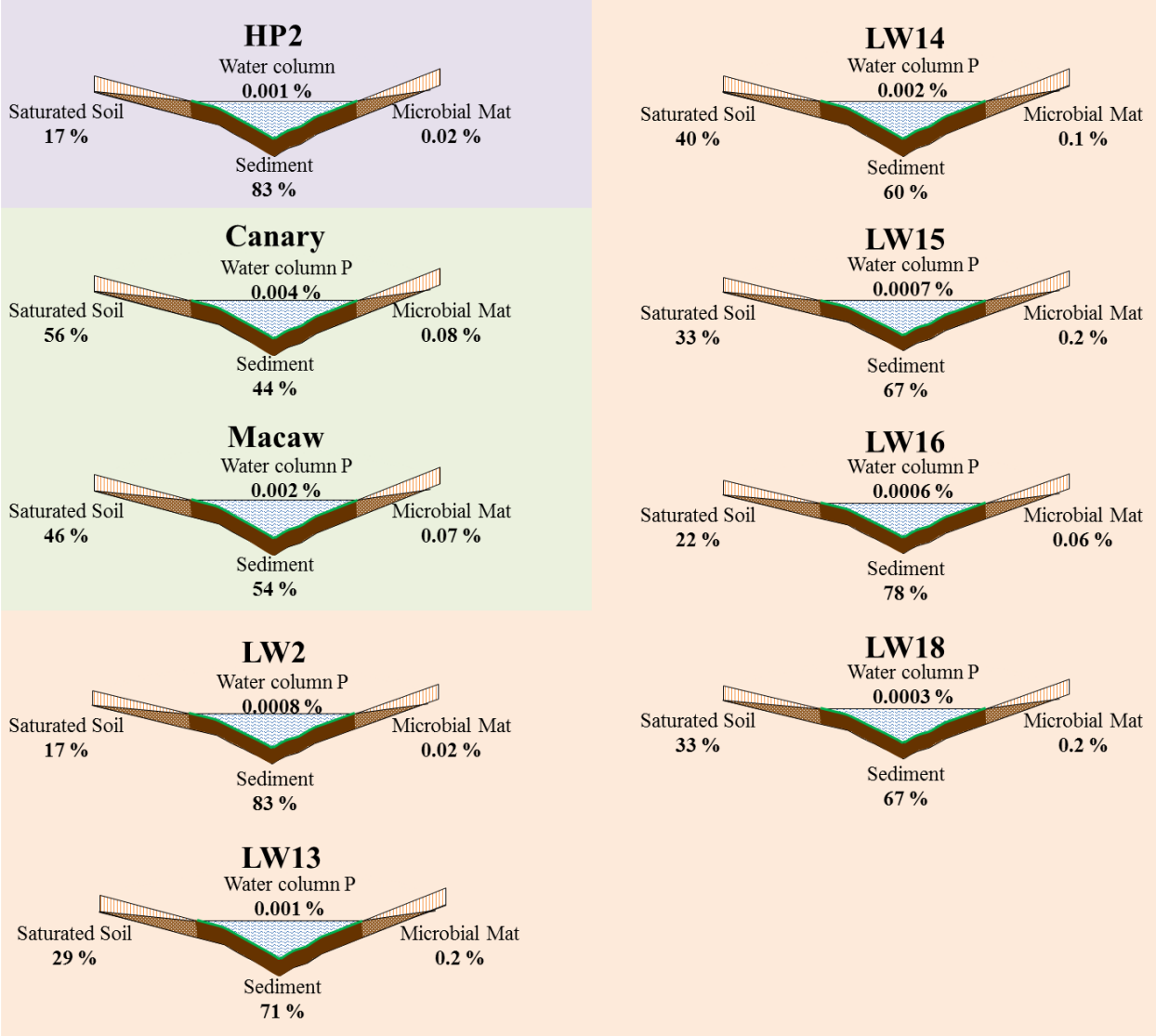


Fig. 5.20 A summary of the percent distribution of P across the 4 reservoirs in the 9 study ponds.

The soil transects at the Miers Valley reveal concentrations of almost every measured fraction of P were lower in the sediment and saturated soil at the pond edge than elsewhere in the pond catchments, using both the Psenner and Hedley fractionation procedures (Fig. 5.18 and 5.19). At Canary pond, Psenner fractionation revealed that the sediments had low exchangeable and apatite P concentrations (Fig. 5.19). Concentrations of both these fractions were higher in soils, and increased with distance from the pond up to 4 m, where they stabilised. This pattern was also seen in the apatite P fraction at Macaw pond. Exchangeable P concentrations at Macaw pond showed a generally increasing concentration from sediments to soils, increasing with distance from the pond, however the saturated soil at the pond edge had the lowest exchangeable P

concentration in the transect. The Hedley fractionation was performed only on the soil samples and shows similar patterns, with the soluble, MO-P and apatite P fractions typically increasing with distance from the ponds (Fig. 5.18). These patterns suggests loss of P fractions in the sediments and the zone of wet soil surrounding ponds, and indicate sediment as a major P source to the ponds. It appears there has also been loss of P in the soils near the pond margins. It is likely that some soil P is transported to the ponds via leaching with snow melt, but it is difficult to quatify the extent to which this, or previous pond levels are responsible for the large concentraion differences seen.

5.5 Summary

This chapter charaterises P abundance and distribution in ponds in several areas of Victoria Land, which range in their geologies and distance from the coast.

Key findings:

- The distribution of P between reservoirs was very similar to the distribution established in the models for inland and costal meltwater systems in Chapters 3 and 4.
- Water column P was generally highest in Ross Island ponds, and lowest in the Lower Wright Valley. Ratios of N:P exceeded the Redfiild ratio in the Lower Wright Valley, indicating possible P limitation, and were less than the Redfield ratio in the Miers Valley and at Ross Island.
- Pond P is predominantly held within the sediments of ponds at all locations, and saturated soil is the second major reservoir.
- Apatite P is the dominant fraction of both soils and sediments, and little P is in a reactive or bioavailable form.
- Sediments typically contain substantially less P than soils, and act as a major P source to ponds.
- The magnitude of the difference between sediment and soil P suggests a pathway for P loss from ponds.

Chapter 6:
Factors driving P distribution and transfer in ponds

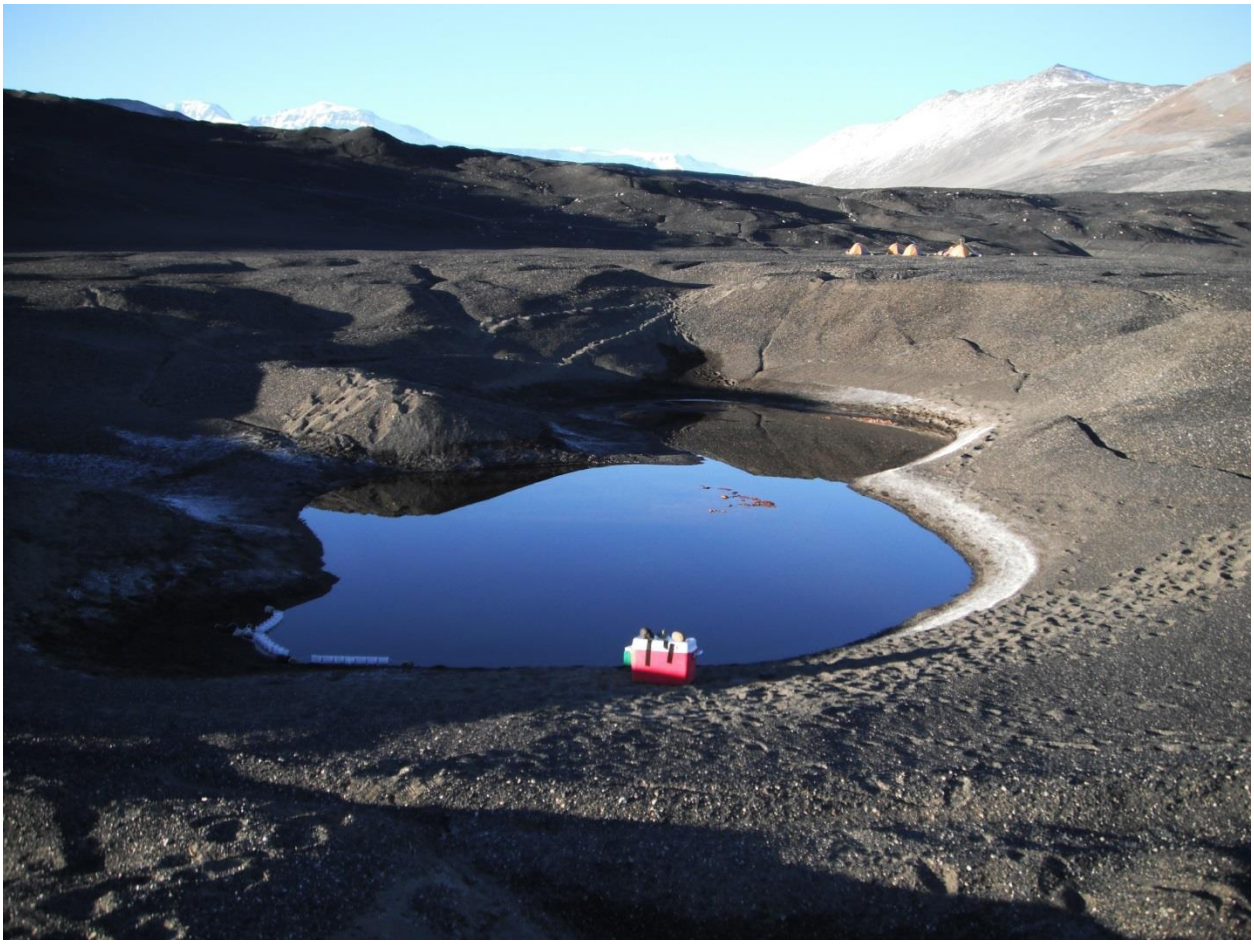


Fig. 6.1 Morepork Pond in the Miers Valley at midnight. The apparatus for the uptake experiments and short term monitoring of pond parameters are set up in the pond, and the field camp can be seen in the background.

6.1 Introduction

Phosphorus is an essential element required for the growth and reproduction of phytoplankton and benthic organisms in aquatic systems. Meltwater ponds in Antarctica are an important habitat for terrestrial life, and there is strong evidence of nutrient deficiency in many pond systems (Vincent & Laybourn-Parry 2008). A general pattern has been observed where coastal aquatic systems have low N:P ratios typical of a nitrogen limited ecosystem, while inland ponds have high N:P ratios indicative of P limitation (Vincent & Howard-Williams 1994, Welch *et al.* 2010).

Pond chemistry is driven by a combination of factors. Catchment geology constrains the contribution of rock weathering to the ponds, and geographical location can affect the composition of aerosols which can deposit soluble salts into pond catchments (Takamatsu *et al.* 1998). Biological processes can alter oxygen concentrations, sulfide concentrations, pH and nutrient concentrations (Hawes *et al.* 2014), and freeze thaw cycles can effect solute distribution and saturation (Wait *et al.* 2009). As discussed previously in this thesis, many factors are also important in determining P chemistry in a pond (Chapters 1-4). None-the-less, distinctive patterns can be seen between meltwater systems at different locations.

Biological uptake of nutrients by both benthic and planktonic communities occurs in polar aquatic systems (Vincent & Vincent 1982, Vincent & Howard-Williams 1986). In shallow systems microbial mats generally dominate biomass, and are a major control on water column nutrient concentrations (Howard-Williams *et al.* 1997, Eichel *et al.* 2014). Determination of nutrient uptake has been used as a tool to assess nutrient deficiency of aquatic systems by coupling uptake with responses in biomass, and has also been used to help predict potential implications of nutrient pulses to aquatic systems (Rigler 1973, Levine & Whalen 2001, Eichel *et al.* 2014). Uptake rates are essential for determining nutrient flux in aquatic systems, and can also inform turnover rates in systems at steady state. Planktonic communities in coastal ponds on Ross Island are typically N deficient, or have sufficient nutrient availability that there is little accumulation of additional nutrients by plankton if they are made available (Vincent & Vincent 1982). In the permanently ice covered Lakes Bonney, Hoare, Fryxell and Vanda, nutrient deficiency indicated by N:P ratios was corroborated by phytoplankton uptake.

Distance from the coast appears to drive some of the differences in chemical composition seen between meltwater systems. This is starkly demonstrated by Welch *et al.* (2010) in streams of the Taylor Valley, where Cl^- dominance of anion chemistry increases, NO_3-N concentrations decrease, and DRP concentrations increase with proximity to the coast (Fig. 6.2). A general trend has been established which shows low N:P ratios in coastal aquatic systems, and high N:P ratios inland (Vincent & Howard-Williams 1994). Glacial tills have a geological legacy effect on soil biogeochemistry, and this also effects P distribution (Bate *et al.* 2008). However, local effects also seem to be important, and nearby ponds can have large differences in conductivity, pH, and chemical compositions (Healy *et al.* 2006, Wait *et al.* 2006, Priscu & Foreman 2009).

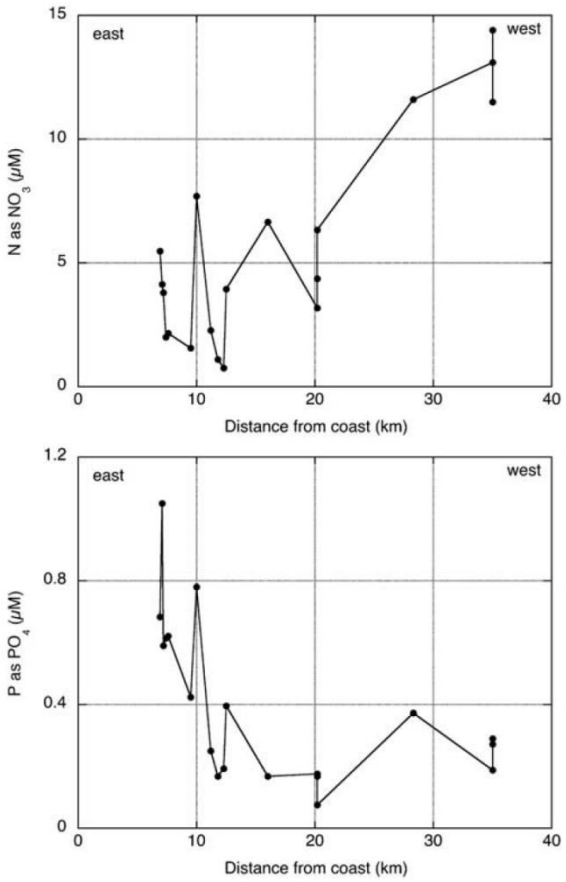


Fig. 6.2 Graphs copied from (Welch *et al.* 2010), which demonstrate DRP and NO_3 concentrations of Taylor Valley streams, as a function of distance from the coast.

Contribution of this research

This thesis set out to answer four key questions about P distribution and cycling in ponds of the Victoria Land regions of Antarctica:

1.3.1 What is the natural abundance of P in each component of a meltwater pond?

1.3.2 What are the sources of P to meltwater ponds?

1.3.3 Is P distribution site specific?

1.3.4 What processes regulate P mobility in these environments?

The abundance of P in key reservoirs of meltwater systems has been demonstrated for ponds at 7 different sample sites in the Victoria Land regions of Antarctica (Chapters 3-5), covering some of the key geologies of the region, as well as examples of coastal, inland and intermediate systems. The sediments have been identified as both the main reservoir of P in meltwater ponds, and a major contributor of P to ponds over their lifetimes.

6.1.1 Chapter Objectives

This chapter will focus on research questions 1.3.3 and 1.3.4, establishing what processes effect P distribution in ponds, and if location alters P abundance and distribution. This will involve:

- Determining factors that regulate water column P concentrations in meltwater ponds, including biological uptake of P, and diurnal cycles
- Comparison of the P abundance and distribution in ponds
- Establishing the effect of location on P chemistry

6.2 Study ponds

This chapter will present data collected on two ponds from Bratina Island that have not previously been described, as well as several other ponds from Bratina Island, the Upper Wright Valley, and the Miers Valley that have been described in Chapters 3 - 5.

Data from all ponds presented in Chapters 3 – 5 are discussed to interpret whether pond location impacts P abundance.

Pond descriptions:

Camp pond

Camp pond is a small pond, 5 m long by 3 m wide and approximately 40 cm deep (Fig. 6.3 a). It is located very close to the New Zealand field camp, to the north of the tide crack at Bratina Island (Fig. 3.2). The pond floor is entirely covered by a smooth, cohesive, olive-green microbial mat. No ice cover or snow bank was present, however a salt margin was present on the southern edge of the pond, and patches of soils salts were present in the catchment.

Ridge pond

Ridge pond is a very small pond 1 m in diameter, and only 10 cm deep (Fig. 6.3 b). The pond floor is entirely covered by an olive green mat with some orange sections, and most of the mat had a layer of small bubbles on its surface. The pond had no ice cover, and no snow was present in the catchment. There was a rim of white soil salts around the pond.

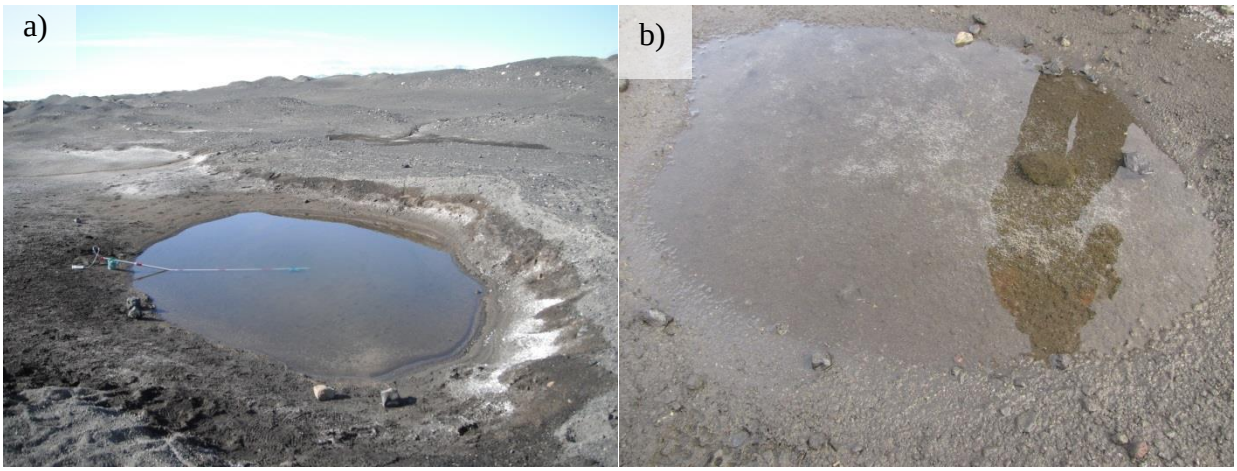


Fig. 6.3 Study ponds at Bratina Island
a) Camp pond b) Ridge pond

6.3 Methods

This chapter will present results from the short term monitoring of meltwater ponds at Bratina Island and the Miers Valley, the microcosm uptake experiments performed at Bratina Island, the Upper Wright Valley, and the Miers Valley, and the *in situ* uptake experiments performed at Bratina Island and the Miers Valley. At Bratina Island, the surface and base of Camp pond was monitored hourly from 08:50 to 20:50, and the surface of Ridge pond was monitored hourly from

18:00 to 24:00 on the 19th January 2013. The weather on the 19th of January was overcast. In the Miers Valley the surface and base of Morepork pond were monitored every 1-2 hours on the 23rd and 24th of January, with some additional measurements taken on the morning of the 25th of January. The weather for these three days was fine with little wind and temperatures of 3 – 6 ºC. For the microcosm uptake experiments, some data points are missing due to either loss of the microcosm during incubation, or sample loss by tube rupture during transport to New Zealand. All methods are detailed in Chapter 2.

The uptake rates calculated in this chapter have used first order reaction kinetics to derive a rate constant, from which an uptake rate can be calculated. In first order reactions, the rate of change in a reactant concentration ([DRP]), is equal to a rate constant (k) multiplied by the DRP concentration (Equation 6.1)(Atkins & Paula 2006). Integrating the first order rate law shows that the natural log of concentration has a linear relationship with time for first order reactions, with a gradient of the rate constant (equation 6.2), where $[DRP]_0$ is the initial DRP concentration.

$$\frac{d[DRP]}{dt} = -k[DRP] \qquad \textbf{Equation 6.1}$$

$$ln[DRP] = -kt + ln[DRP]_0 \qquad \textbf{Equation 6.2}$$

Where uptake occurred that obeyed these kinetics, uptake rates were calculated by performing a linear regression on the natural log of the DRP concentration at each time interval. The resulting gradient gave a rate constant value (k), which when multiplied by a DRP concentration, gives the uptake rate at that concentration. The cores used for the microcosm uptake experiments were 6 cm in diameter, which enabled an uptake rate per unit area to be calculated. This allowed DRP uptake to be estimated for several ponds. Few ponds had uptake patterns which consistently displayed first order kinetics over the uptake experiment period, and concentration fluctuations indicated DRP release to also occur. Additionally, the triplicates did not always behave consistently. Therefore estimates of DRP flux are anticipated to be in the same order of magnitude as the actual uptake.

6.4 Results

6.4.1 Diurnal patterns in meltwater ponds

The 5 main parameters measured in Camp pond over 12 hours all showed variation with time, both at the surface and the base of the pond (Fig. 6.4). Temperature was typically slight warmer at the pond surface, and increased from 0.2 ºC at the pond base at 08:45, up to a maximum 6 ºC at the surface at 16:45. The dissolved oxygen concentration was generally higher at the base of the pond, and decreased from 14.57 mg/L at 09:45 to 13.93 mg/L at 13:45 (base), after which time the surface and base concentrations fluctuated by up to 0.4 mg/L between readings. The % saturation of DO was above 100 for the duration of sampling. The % saturation at the pond base increased from 105 % at 09:45 (at 08:45 the pond water was too cold for the meter to read), up to 112.3 % at 17:45, after which it declined to 109 % at 20:45. The surface % saturation of DO had a similar pattern, however at 17:45 the % saturation decreased sharply to 109 %. Pond pH was generally higher at the base of the pond, which decreased from 8.45 at 08:45 to 8.29 at 12:45, before rising again to 8.38 at 20:45. The surface pH showed a similar pattern, and at 15:45 pH at the pond base and surface decreased to the minimum values measured. DRP concentrations at the base of the pond ranged from 0.001 to 0.017 mg/L, and fluctuated widely hour to hour. At the pond surface, the DRP concentration also fluctuated, however from 09:45 to 15:45 the DRP concentration increased steadily from 0.002 to 0.009 mg/L. Conductivity initially decreased, then gradually increased throughout the day, both at the surface and the base of the pond.

At Ridge pond, the temperature steadily decreased from 6.6 ºC at 18:00 to 1.5 ºC 24:00 (Fig. 6.5). The % saturation of DO also decreased during this time; however the DO concentration was stable until 20:00, and then decreased. The water pH of approximately 8.72 was fairly stable over the 6 hours. DRP concentrations varied nearly 3 fold from 0.0034 to 0.0089 mg/L. Conductivity dropped from 5.79 to 5.62 mS/cm over the study period.

At Morepork pond in the Miers Valley, the temperature varied from 4 – 9.6 ºC (Fig. 6.6). The temperature at the base of the pond was lowest at 08:45, and greatest at 14:45, while at the surface the minimum temperature was recorded at 03:30, and the highest at 16:50. Dissolved oxygen concentrations fluctuated from 12.79 to 13.79 mg/L and did not show a consistent pattern with time, however the surface % saturation of DO showed a similar pattern to temperature. The

water was always over saturated with DO, ranging from 103.9 % at 03:30 to 122.7 % at 18:50 on the pond surface. Pond pH was consistently close to 9.4, however a diurnal cycle did appear to exist, with increasing pH values between midnight and 10:00, and slowly decreasing values thereafter. DRP concentrations were very low, and varied from 2 to 4 µg/L. No clear pattern was evident over the day. Conductivity seemed to vary with time, with the maximum value of 4.29 ms/cm recorded at 03:30, and the minimum of 3.92 at 13:50.

6.4.2 *In situ* uptake of DRP

In situ uptake experiments were undertaken at Orange Pond at Bratina Island, and in Finch and Morepork Ponds in the Miers Valley. At Orange pond, 2 µg/L or less DRP was present in the containers at the time zero sampling, and in the water of the transparent containers after 48 hours incubation (Table 6.1). In the dark containers however, DRP concentrations of 4 and 6 µg/L were measured after 48 hours. At Morepork pond, 1-2 µg/L DRP was present at time zero. In the transparent containers, DRP concentrations of 3 and 6 µg/L were measured after 62 hours, while water in the dark containers had 16 and 22 µg/L of DRP. In Finch pond, time zero concentrations ranged from 3 – 6 µg/L, and interestingly one of the dark and transparent containers had an increased and a decreased concentration after 48 hours.

Table 6.1 DRP concentrations of water during *in situ* uptake experiments in ponds at Bratina Island and the Miers Valley. The values with a * were measured after 62 hours of exposure time, rather than 48 hours, and <dl represents a value was below the detection limit of 1 µg/L.

Pond	Condition	DRP t=0 (µg/L)	DRP t=48 (µg/L)
Orange	Light	<dl	<dl
		<dl	<dl
	Dark	<dl	6
		2	4
Morepork	Light	1	3*
		2	6*
	Dark	1	16*
		1	22*
Finch	Light	6	12
		5	3
	Dark	4	3
		3	12

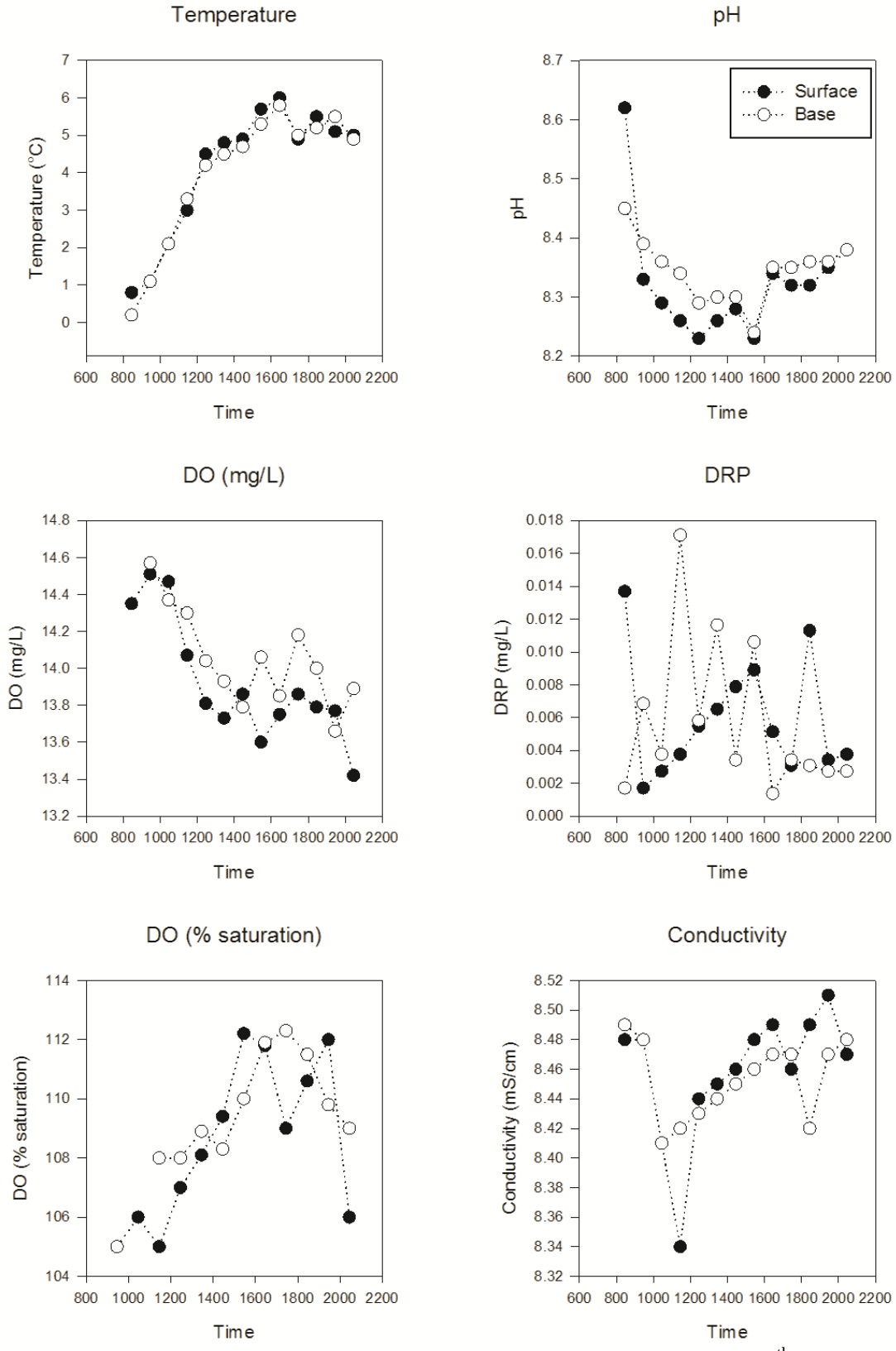


Fig. 6.4 Short term monitoring data for Camp pond, Bratina Island, on the 19th January 2013 (12 hour observation period)

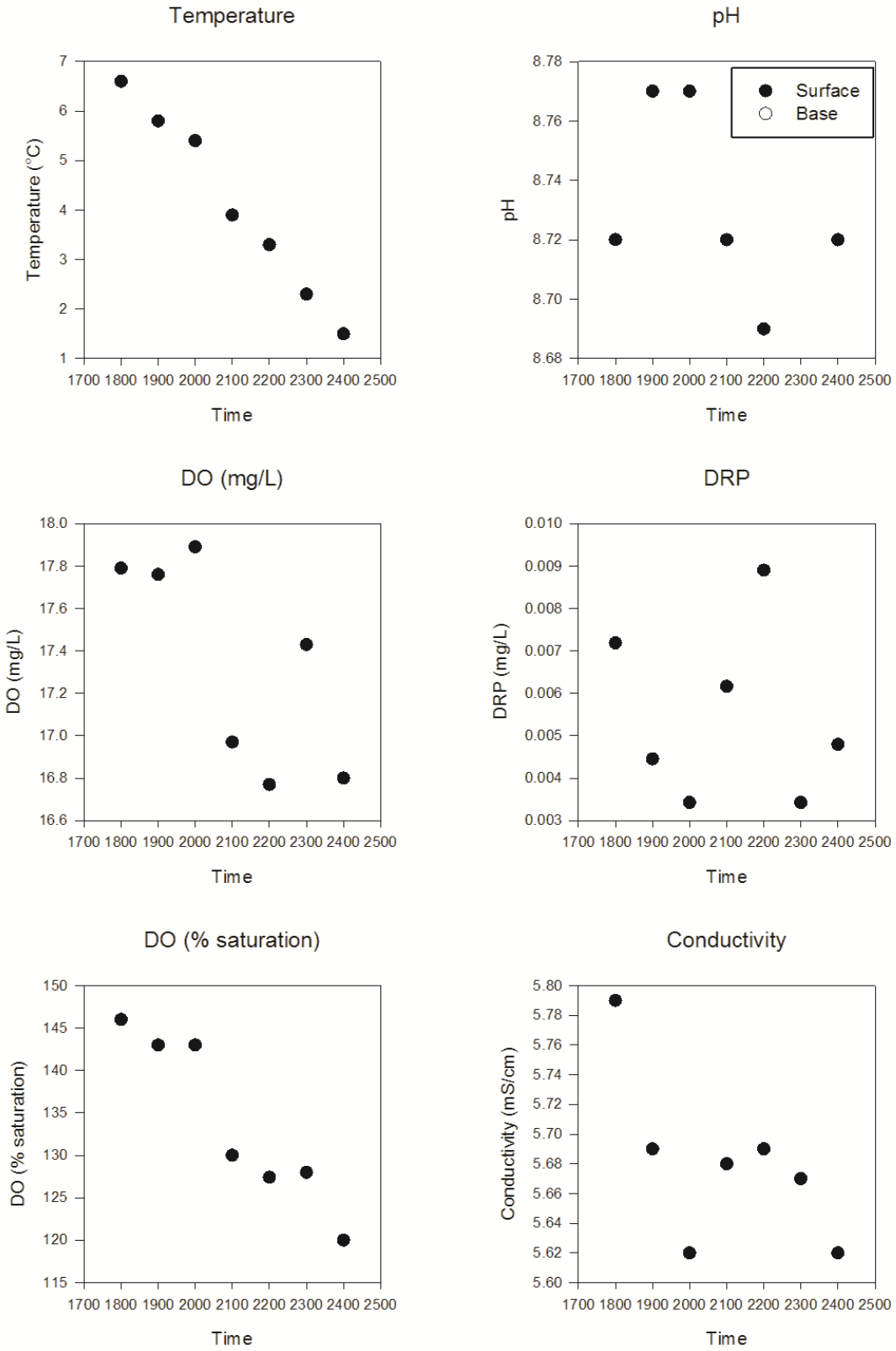


Fig. 6.5 Short term monitoring data for Ridge pond, Bratina Island, on the 19th January 2013 (8 hour observation period)

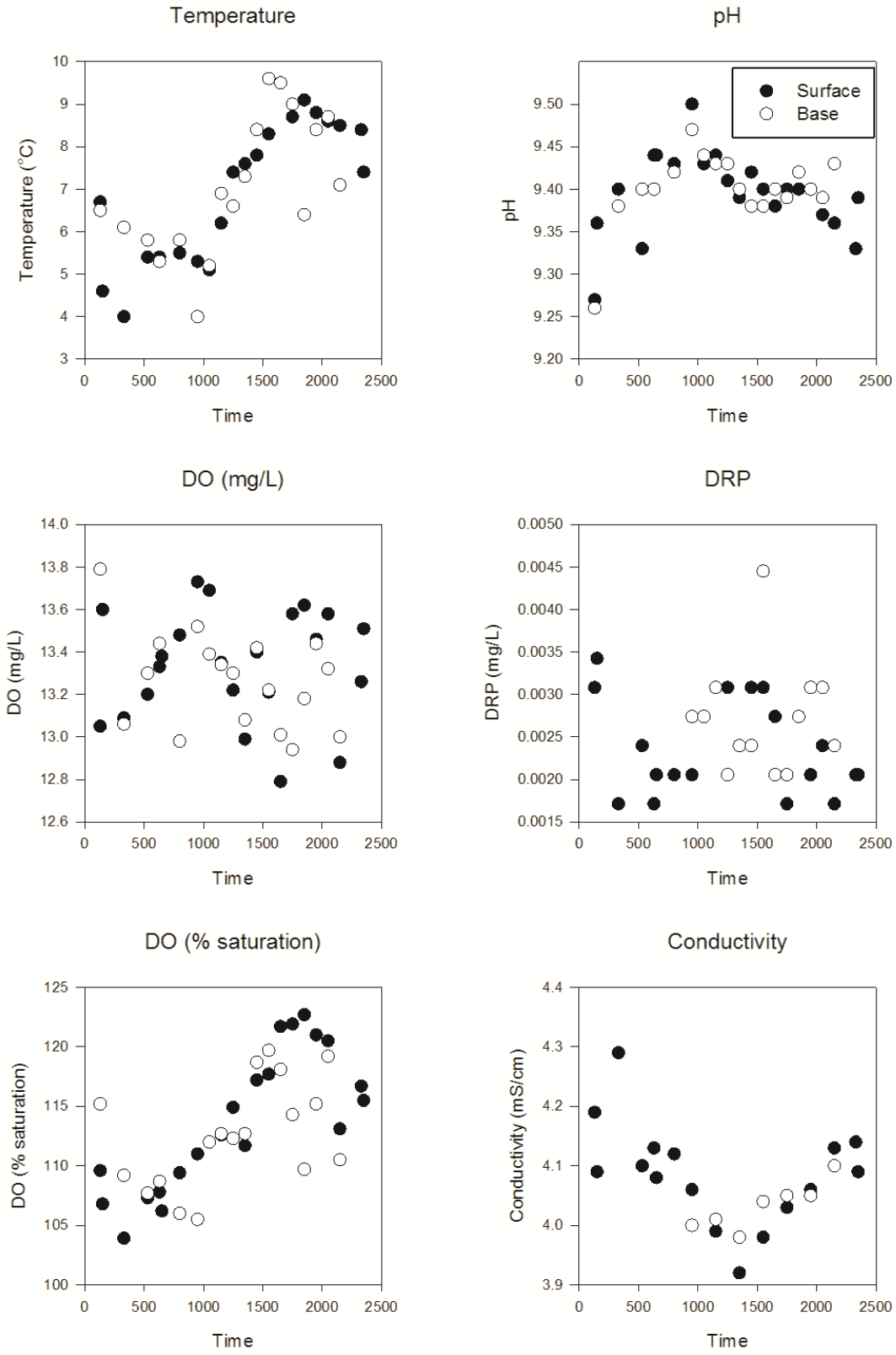


Fig. 6.6 Short term monitoring data for Morepork pond, Miers Valley, from the 23-25th January 2013 (24 hour observation period)

6.4.3 DRP Uptake in microcosms

The DRP concentrations in the microcosms spiked with 50 µg/L DRP typically decreased over the 24 - 48 hour observation period (Fig. 6.7, 6.8). The Orange pond samples showed a decrease in DRP concentration over the first 8 hours, except for the control microcosm with no microbial mat, where concentrations remained high (Fig. 6.7). In the Salt pond microcosms, a rapid decrease in DRP concentration was observed during the first 8 hours, which seemed to stabilize thereafter. This was observed in the three replicates with mat, as well as in the control with no mat added. Skua pond, which had the highest water column DRP concentrations at Bratina Island, showed an overall decrease in DRP concentration over the 48 hour incubation, however concentrations fluctuated significantly within this time frame. Similar results were observed in the microcosms spiked with 5 µg/L DRP, where DRP concentrations typically decreased over the observation period (Fig. 6.9). In both Salt and Orange ponds however, some fluctuations in DRP concentration were observed.

In the Miers Valley, DRP concentrations in the 50 µg/L spiked microcosm from Canary pond behaved differently (Fig. 6.7). DRP concentrations unexpectedly increased during the first 8 hours, and typically decreased thereafter. The 50 µg/L spiked samples from Finch and Morepork ponds showed decreasing DRP concentrations over the observation period, with some fluctuations in the control sample DRP concentrations. The 5 µg/L spiked microcosms from Canary pond also showed surprising results, with DRP concentrations increasing over the initial 4 hours, then decreasing in two of the replicates, and further increasing in the third replicate (Fig. 6.9). At Finch pond, the 5 µg/L spike microcosms also showed increasing DRP concentrations initially, concentrations then decreased in the 24 hour sample, and increased again in the 48 hours sample. The Morepork microcosms showed increasing DRP concentrations throughout the observation period.

In the experiments performed on samples from the Upper Wright Valley, the 5 µg/L spiked samples had <3 µg/L DRP present, indicating depletion of the added nutrient. The detection limit for these samples was slightly higher than those from other sites due to analysis on a different spectrophotometer. The samples that were spiked with 50 µg/L DRP had an initial rapid decline in DRP concentration. In Fig. 6.8 the initial concentration was not measured, however as the

ponds had <1 – 2 μg/L DRP in the water column, the amended concentration of 50 μg/L is included on the graph. Similar behavior was observed in most of the replicates, however at L26 pond, an apparent release of DRP occurred in two of the containers after 1 hour, after which continued decrease in concentration was observed.

The fluctuating concentrations made it difficult to establish uptake rates of DRP in all of the ponds, however in some ponds first order reaction kinetics were evident (Table 6.2, Appendix 2). Where a linear regression of the natural log of concentration over time had a correlation coefficient where $R^2 > 0.7$, an uptake rate was calculated. In Salt pond, for the first 8 hours of the experiment the natural log of the DRP concentration decreased linearly with time, with R^2 values ranging from 0.72 – 0.99. Rate coefficients allowed calculation of expected uptake rates in the pond water, which ranged from 0.07 – 9 mg m^{-2} h^{-1} at the natural pond DRP concentration. The rate coefficient was greatest in Salt pond, and lowest in Orange pond (0.04 – 0.3 h^{-1}), with constants for ponds from other areas falling within this range. The highest rate of DRP uptake was in Skua pond where the highest DRP concentration was measured. The estimated fluxes for DRP uptake ranged from 3 – 1500 mg P per hour, with the lowest value at Finch pond in the Miers Valley, and the highest at Skua pond on the McMurdo Ice Shelf.

Table 6.2 An assessment of the kinetics demonstrated in the microcosm uptake experiments performed at Bratina Island, the Miers Valley, and the Upper Wright Valley, and associated uptake characteristics derived from these.

Pond	First order kinetics met?	Concentration with clearest kinetics	R^2 range	Average rate constant ($R^2 > 0.7$, h^{-1})	Pond DRP (mg/m^3)	Uptake rate (mg $P/m^2/h$)	Pond DRP flux (mg/h)	Pond DRP flux g/day
Salt	Yes	50	0.72-0.99	0.3	0.022	2	900	20
Orange	In 2/3 microcosms	50	0.50-0.82	0.04	0.097	1	200	5
Skua	Yes	5	0.75-0.92	0.06	0.44	9	2000	40
Morepork	No	-	<0.5	-	-	-	-	-
Finch	Yes	50	0.77-0.92	0.05	0.004	0.07	3	0.07
Canary	No	-	<0.5	-	-	-	-	-
E4	Yes	50	0.68-1	0.05515	0.002	0.04	100	2
L16	No	-	0.08-0.4	-	<1	-	-	-
L26	In 1/3 microcosms	50	0.09-0.90	0.117	<1	0.02	6	0.1

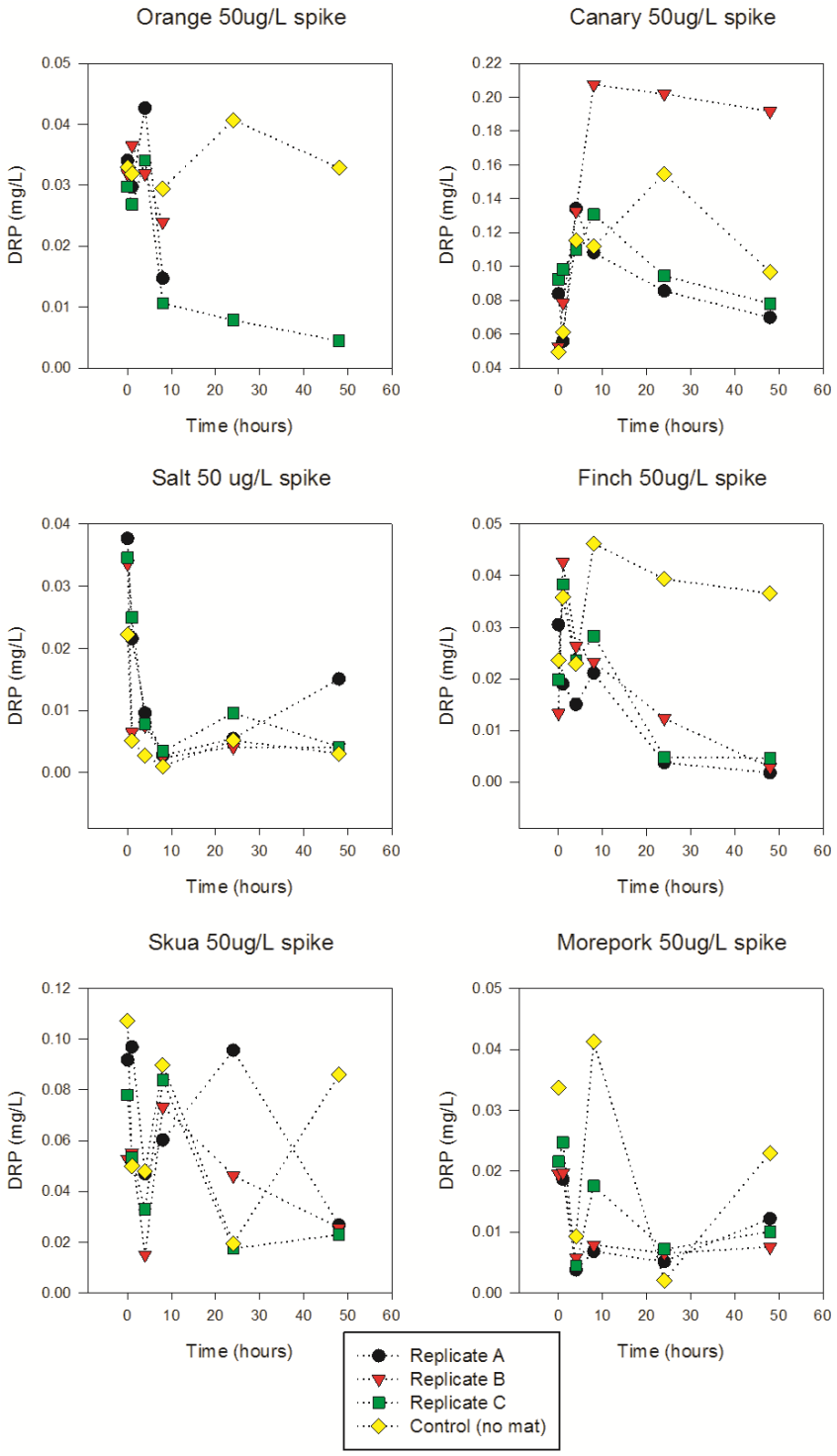


Fig. 6.7 DRP concentrations in microcosms containing mat and water from each named pond from the McMurdo Ice Shelf and Miers Valley. Each microcosm was spiked with 50 µg/L DRP.

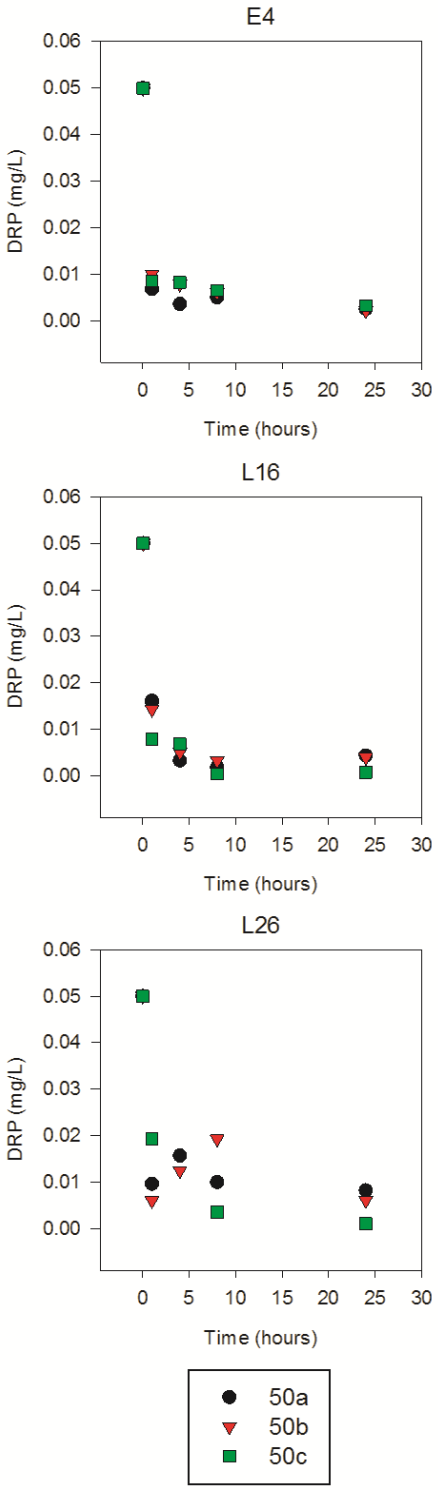


Fig. 6.8 DRP concentrations in microcosms containing mat and water from each named pond from the Upper Wright Valley. Each microcosm was spiked with 50 µg/L DRP, which has been included as the initial DRP concentration. Controls were performed for a 5 µg/L spike where concentrations were below detection.

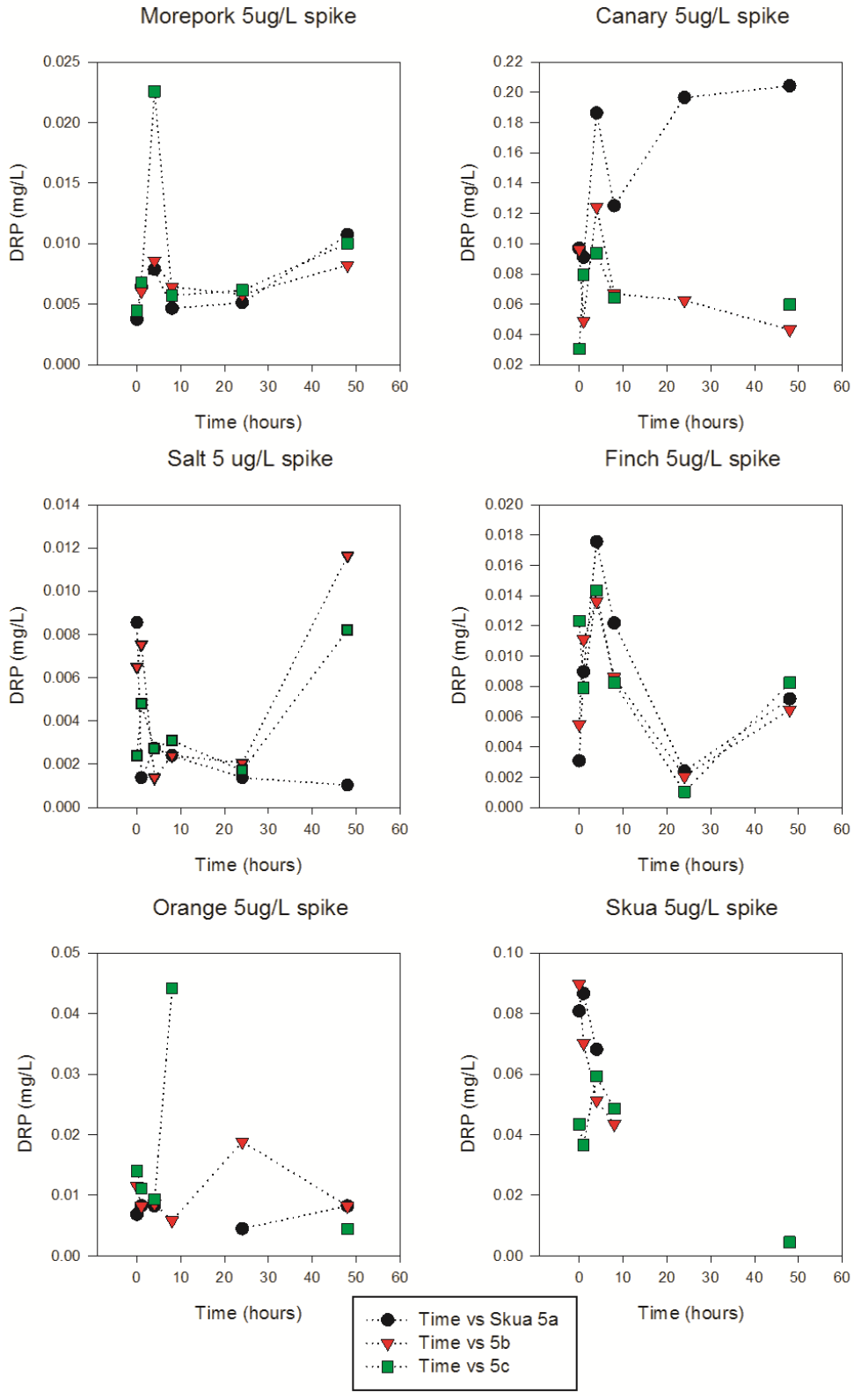


Fig. 6.9 DRP concentrations in microcosms containing mat and water from each named pond from the McMurdo Ice Shelf and Miers Valley. Each microcosm was spiked with 5 µg/L DRP.

6.5 Discussion

6.5.1 Diurnal patterns in ponds

The short term monitoring of meltwater ponds revealed that diurnal physical and chemical changes occur in the ponds. Water temperature is perhaps the most obvious parameter that will change, and the changes that we see in DO concentration and saturation are likely partially driven by temperature change. Conductivity in Camp pond was not monitored long enough for a clear trend to become apparent. In Morepork Pond conductivity decreased throughout the morning, and then increased in the afternoon and evening. Changes in temperature could drive evaporation, change activity of ions in the pond water, or cause mixing by changing water density, however as no correlation with temperature occurs (Appendix 3), another mechanism is likely to be responsible for the conductivity changes.

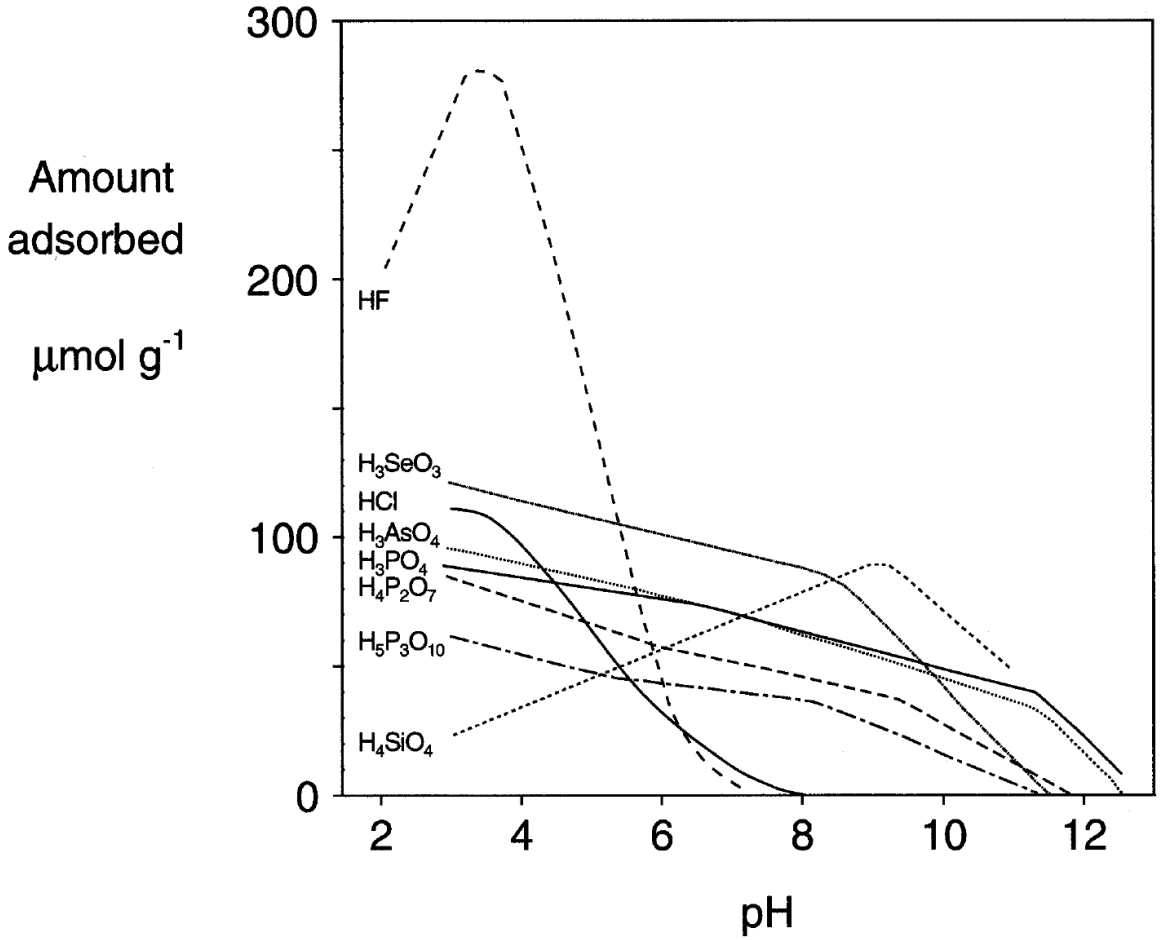


Fig. 6.10 The effect of pH on the adsorption of anions on goethite, modified from Cornell and Schwertmann (2006).

In Camp Pond, the surface DRP concentration increased over the day, however at the base there were considerable fluctuations in DRP concentration. DRP release from the microbial mat may be the cause of the large fluctuations, as phytoplankton release of DRP might be expected to occur throughout the water column. High pH can drive desorption of phosphate from metal oxides (Fig. 6.10), and the pH variations observed in the ponds (up to 0.4) could alter DRP concentrations via adsorption reactions on metal oxide surfaces (Cornell & Schwertmann 2006). No correlation was seen between pH and DRP concentration however, so diurnal pH change does not seem to be the dominant driver of the observed DRP changes, though may act as a non-dominant driver. In all 3 ponds monitored, DRP concentrations varied by at least a factor of two over the monitoring period. These results indicate water column DRP concentrations in meltwater ponds are dynamic. The lack of correlation to any physico-chemical parameter suggests that the rapid changes are biologically driven. The greater variability in DRP concentrations at the base of Camp Pond indicates DRP release is most likely from the microbial mat.

6.5.2 Uptake of DRP

The microcosm DRP uptake experiments demonstrated that DRP is sequestered from the water column by the microbial mat, even in the coastal areas which have relatively abundant DRP. Greater DRP concentrations seemed to drive faster uptake rates as predicted by the rate law. However, the apparent release of DRP in some microcosms made it difficult to calculate uptake rates, as DRP concentrations did not follow a pattern typical of established reaction kinetics. The DRP concentration in nearly every microcosm spiked with 50 μg/L DRP decreased over the observation period, and greater decreases were typically observed in the microcosms which also contained microbial mat. Concentration decreases in the control microcosms suggest phytoplankton are also responsible for some DRP removal from the water. At Salt Pond phytoplankton seem to be the major component removing P from the water, with similar decreases in DRP observed in the control and mat containers. Fluctuations in the DRP concentrations are likely due to DRP release and re-sequestration, as appeared to occur in the ponds observed in the short term monitoring. Although no correlation was seen in the short term monitoring, pH can mediate P release, and if the experiment was to be repeated pH would be measured over the time course. Large DRP concentration fluctuations occurred in the control

microcosms as well as those with microbial mat, indicating that rapid DRP release and uptake seems to occur both by phytoplankton and microbial mats.

The fluctuating concentrations observed in some of the microcosms were unexpected, and such variations have not been reported in other uptake experiments performed in the region. Rather, nutrient concentrations generally stay near the initial value, or decay over time (Vincent and Howard-Williams, 1986). Some of the microcosm uptake results appear almost contradictory, for instance in Morepork pond, the 50 μg/L microcosms appeared to draw down DRP, while in the 5 μg/L microcosms DRP was released. In general, the 5 μg/L microcosms showed increased variation relative to the initial concentration, compared to the 50 μg/L microcosms. During the 8 hour short term monitoring of Camp pond, DRP concentrations varied from 1 – 17 μg/L, a similar range to the variations observed in most of the 5 μg/L spiked microcosms (1 – 23 μg/L range for all but Canary pond). Therefore, the fluctuating DRP concentrations observed throughout the experiment in some of the microcosms is likely due to DRP release and uptake that can occur in ponds throughout the day.

The calculated uptake rates ranged from 0.02 – 9 mg/m^2/h DRP, and were in a similar range to the saturated uptake rates calculated for microbial mats in the Onyx River (0.7 – 8 mg / m^2/h DRP)(Howard-Williams *et al.* 1997). This corresponded with DRP flux values in the order of 0.07 to 40 g of P being taken up by pond biota each day. The short term monitoring revealed fluctuations in DRP concentration can occur rapidly in ponds, and DRP concentration in different locations within a water column are not always constant, even when conductivity stratification is not present. This illustrates that DRP uptake is not in equilibrium with DRP release, though overall a steady state is likely maintained. DRP can be returned to the water column via four main pathways: direct release from cells, excretion from grazers, pH mediated release and enzymatic hydrolysis of organic P molecules released during excretion, cell lysis or decomposition (Rigler 1973). Isotope tracing techniques allow effective calculation of turnover rates, and would be a good tool to apply to these systems to establish flux for biological P transfer pathways.

The *in situ* uptake experiments also show that during lit conditions in summer the mat can act as both a source and a sink of DRP to the water column. In dark conditions, mats appear to act

principally as a DRP source to pond water, with all but one of the dark containers having at least double the initial DRP concentration after the incubation period. Meanwhile, the transparent containers typically showed only slightly increased or decreased DRP concentrations relative to the initial DRP concentration. Microbial mats are nourished by DRP which they can sequester from the water column and from sediment pore water, and can also reduce nutrient permeation from sediments to the water column (Hansson 1988). In summer growth conditions, microbial biomass increases via photosynthesis, which consumes inorganic compounds. In simple terms, we may consider photosynthetic production, and heterotrophic respiration to be described by the following equation assuming Redfield stoichiometry (Redfield 1958, Stumm & Morgan 1996):

$$\mathbf{16}\,NO_3^- + \mathbf{124}CO_2 + \mathbf{140}H_2O + HPO_4^{2-} \leftrightarrow C_{106}H_{263}O_{110}N_{16}P + \mathbf{138}O_2 + \mathbf{18}HCO_3$$

Equation 6.3

Respiration is the reverse process, and it is logical that under dark conditions DRP was released from the mats. This process has implications for seasonal effects on P in the ponds. As less photosynthetically active radiation enters ponds, respiration will become the dominant process, likely leading to increased DRP concentrations in the pond water entering winter. In addition, freeze-thaw cycles cause DRP and DOP release from microbial mats, and it is therefore likely that as the pond thaws in summer, a pulse of dissolved P will be present in the water column.

6.5.3 Influence of location on P dynamics

For all ponds studied in this thesis, distribution of P across the major reservoirs was similar (Table 6.3). Sediments were the major reservoir in all but one pond, followed by saturated soils, while the mat and water column held orders of magnitude less P. The relative volume of each reservoir is dependent on pond size, and in the large ponds of the Labyrinth in the Upper Wright Valley, the saturated soil reservoir was typically small relative to the sediment reservoir. Volume is clearly proportional to the P content, and therefore, despite soils in the Labyrinth having similar P concentrations to the sediments, the P content of the saturated soil reservoir is much less than the sediment reservoir.

Despite similarities in P distribution, the abundance and availability of P was variable between sites. A comparison of average pond DRP and TP concentration at each sample site indicates that

ponds from different locations have very different P abundances. Data collected in this study supports previous research showing increased P concentrations in coastal aquatic systems in Antarctica, and very low P concentrations in inland systems. This observation across sample sites held true for the average total P concentration in all pond reservoirs, with a general pattern of Bratina Island > Ross Island ≈ Miers > Lower Wright Valley > Upper Wright Valley (Fig. 6.11). Similarly, the concentrations of particular fractions of P in many of the systems also followed this pattern.

Table 6.3 The ranges of P distribution across reservoirs in ponds at each study site

Area	Sediment (%)	Soil (%)	Mat (%)	Water (%)
MIS	65-83	16-34	0.004-.01	0.001-0.01
UWV	83-97	3-17	0.04-.05	0.0004-0.02
LWV	60-83	17-40	0.01-.02	0.0003-0.002
HPP	83	17	0.004	0.001
MV	44-54	46-56	0.02	0.002-0.003

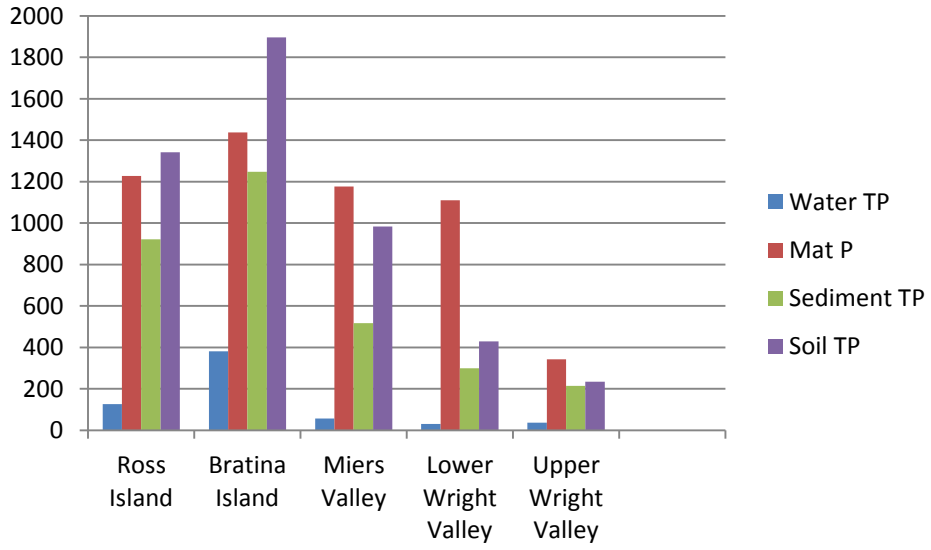


Fig. 6.11 The average total P concentration in the reservoirs of the study ponds at each sample site.

At all sites, soil and sediment P was dominated by apatite P, which comprised 84 – 98 % of the total P at all study ponds. This is consistent with other P fractionation work completed in the Victoria Land region (Blecker *et al.* 2006, Bate *et al.* 2008). In sediments, for which the Psenner extraction scheme was used, the metal oxide adsorbed fraction (MO-P) was the next most dominant fraction at Bratina Island and in the Miers Valley, however reducible oxide adsorbed P (RO-P) was relatively higher in the Wright Valley ponds. At HP2 on Ross Island, the concentrations of both MO-P and RO-P were very similar. Reducing conditions have been documented in ponds of the McMurdo Ice Shelf (Wait 2011), and H_2S gas was present in basal samples in the Miers Valley, as well as noted in some sediments. Dissolved oxygen concentrations were measured in the basal brine of ponds in the Upper Wright Valley in October 2004, and although low temperatures interfered with the oxygen probe, all brines contained detectable oxygen (Healy *et al.* 2006). No H2S was found in the brines (Healy *et al.* 2006), however it is possible that at some periods during the year the basal brine is deoxygenated, and may subject the sediments in the deepest part of the ponds to reducing conditions. It is likely that the bulk of pond sediments in the Upper Wright Valley do not experience reducing conditions. In the Lower Wright Valley, a slight H_2S smell was noted in one of the cores taken from LW16 pond. It is possible that an absence of reductants allow higher concentrations of reducible oxides to persist in the sediments of ponds in the Wright Valley, resulting in greater RO-P relative to MO-P. Alternatively, the high N:P ratios for these areas may result in increased demand for organic P species which are included in the MO-P fraction.

Sediments appear to be a major contributor of P to ponds, and consistently contained between 20 and 50 % less total P than was found in soils near the ponds. At Bratina Island the mineralogy of a soil and a sediment sample from Fogghorne pond were nearly identical, and hence it is assumed that for most ponds, soils and sediments had similar P composition prior to the sediment becoming inundated. Therefore, the consistently low P concentrations in sediments relative to soils demonstrate significant loss of sediment P to the pond over time at most of the sample sites. The two exceptions are in the Labyrinth, where historic pond levels and the formation processes may have caused significant leaching of soil P prior to sampling. At Hut Point Peninsula, only HP2 pond was sampled for sediment, which had a much higher total P concentration than the Ross Island soils. The proximity of this pond to historic and current anthropogenic influences may have some impact on the pond. Due to the overwhelming similarity in sediment versus soil

P concentrations at the other sites, HP2 is being considered unusual and further characterization of Ross Island sediments is required.

Water column chemistry showed variation within and between sites. Water column P was generally dominated by PP in ponds, however at most sites there were ponds in which DRP or DOP was the major form. Pond DOP can reach very high concentrations, such as the 724 µg/L that was measured in Salt pond in 2011. On the McMurdo Ice Shelf log transformed DOP and DON concentrations correlate with conductivity over time, as a result of refractory compounds behaving conservatively in the water column (Hawes *et al.* 2014). In this work, no overall correlation was observed between DOP concentrations and conductivity (Fig. 6.12), suggesting perhaps a source of refractory DOP to ponds on the McMurdo Ice Shelf, or an increased capacity to recycle organic P in ponds in other locations.

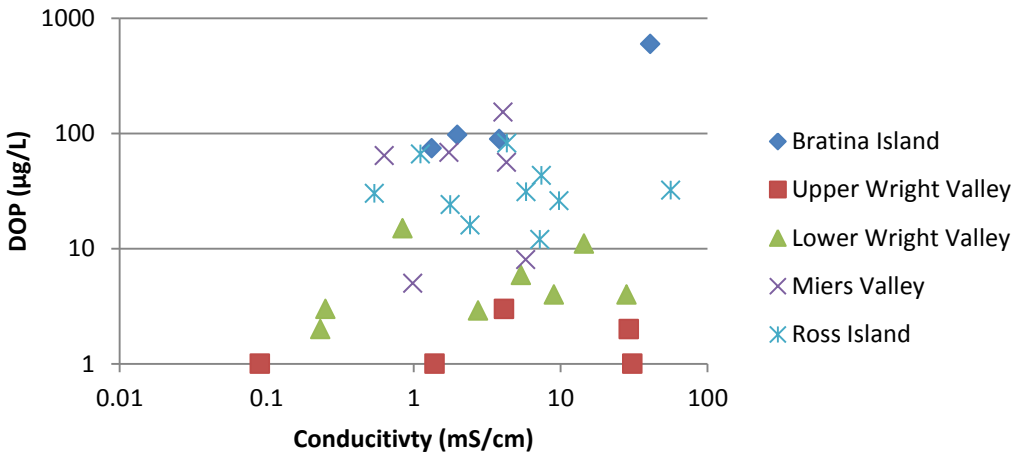


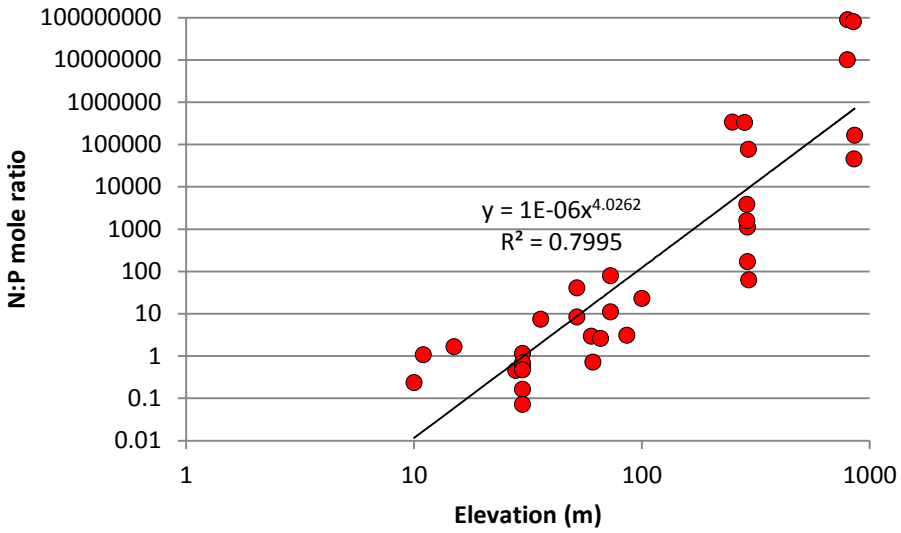
Fig. 6.12 A graph of the surface conductivity versus the DOP concentration in the water column of study ponds at each sample site.

In contrast to the DRP concentrations, dissolved inorganic nitrogen (DIN) concentrations were low in systems near the coast and high inland. This distribution supports previous findings, and is likely due to deposition of stratospheric NO_3^- aerosols (Vincent & Howard-Williams 1994). Ratios of inorganic N:P were correspondingly very low near the coast, and very high inland. Log transformed N:P ratios correlated more strongly with elevation than with distance from the coast, with R^2 values of 0.80 and 0.26 respectively (Fig. 6.13).

Green Lake at Cape Royds had anomolously high N and P concentrations for the area, which are likely due to seabird guano. These high concentrations seemed to nourish a productive phytoplankton community, evident from the turbid green water and high particulate N and C concentrations. The C:N:P ratios of the particulates were very P rich compared to all other ponds in the area, indicating an analytical error in the PP determination for Green lake. Other large ponds in the Cape Royds study area were also frequented by resident penguin and skua, and these included 'Pony Lake' directly adjacent to the penguin rookerie, and an un-named pond which many skua were nesting by. In general the ponds at Cape Royds had higher DIN concentrations than the other study ponds on Ross Island, which may be due to seabird contribution. This supports findings that phytoplankton in some coastal ponds of Ross Island are not deficient in either N ir P (Vincent & Vincent 1982).

In addition to the nutrient results, relative major ion composition of the study ponds also varied with location. For cationic composition, most ponds from the same location had similar ratios of Na + K to Mg, indicating a common source of these ions to the pond systems (Fig. 6.14). This was particularly evident in ponds of the Upper and Lower Wright Valley, where Na + K to Mg ratios were approximately 2 and 5 respectively. In these ponds, the relative concentration of Ca was variable, indicating a process local to each pond which may act as a source or sink of Ca. Examples of such local processes may be precipitation of a Ca bearing salt due to oversaturation in the pond water at some stage in the annual cycle, as has been evidenced in the Upper Wright Valley, where gypsum was predicted to precipitate during winter, and found in the base of some ponds. Ponds from Ross Island typically had cation compositions close to standard seawater (Millero *et al.* 2008), and were the only site where compositions were all very similar. In the Miers Valley ponds, ratios of Mg to Ca were close to 1.5, and the relative concentration of Na + K was much more variable. The eastern basin of the Miers Valley contains mirabilite thought to be formed during freeze concentration of a water body containing seawater derived sulfate (Lyon 1978). Patchy distribution of this soluble salt in the area may be the cause of varying Na concentrations.

a)



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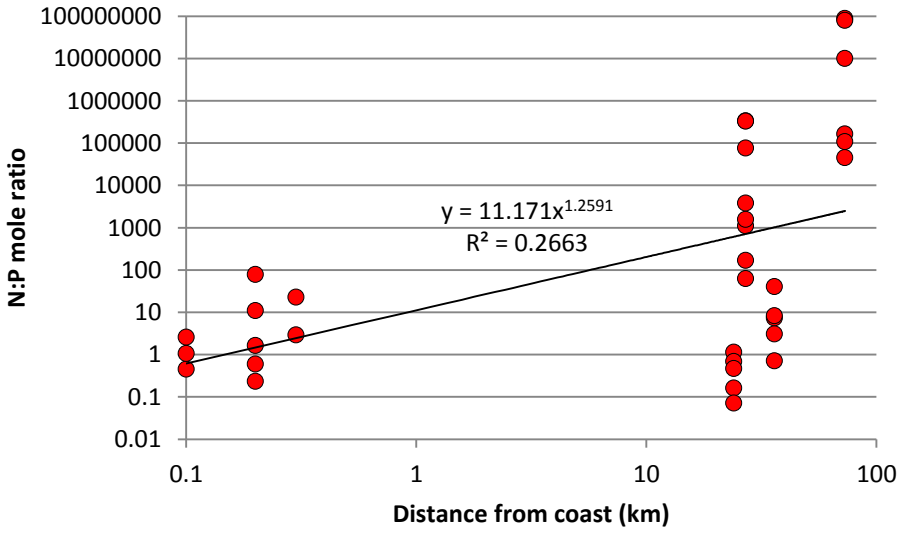


Fig. 6.13 Graphs of the inorganic N:P mole ratio versus **a)** elevation and **b)** distance from coast.

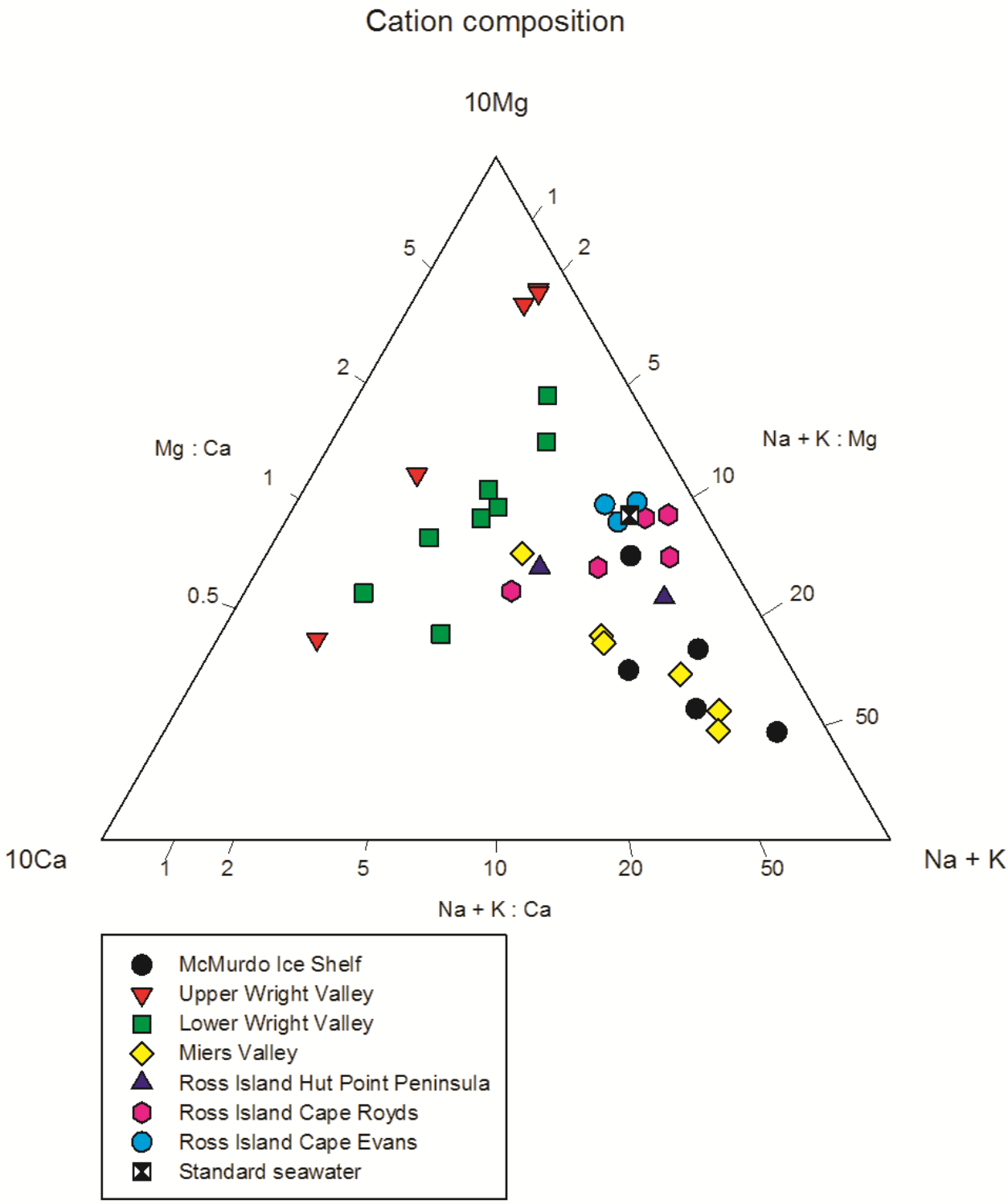


Fig. 6.14 Molar cation composition of pond waters at each sample site, as well as standard seawater for comparison (Millero *et al.* 2008).

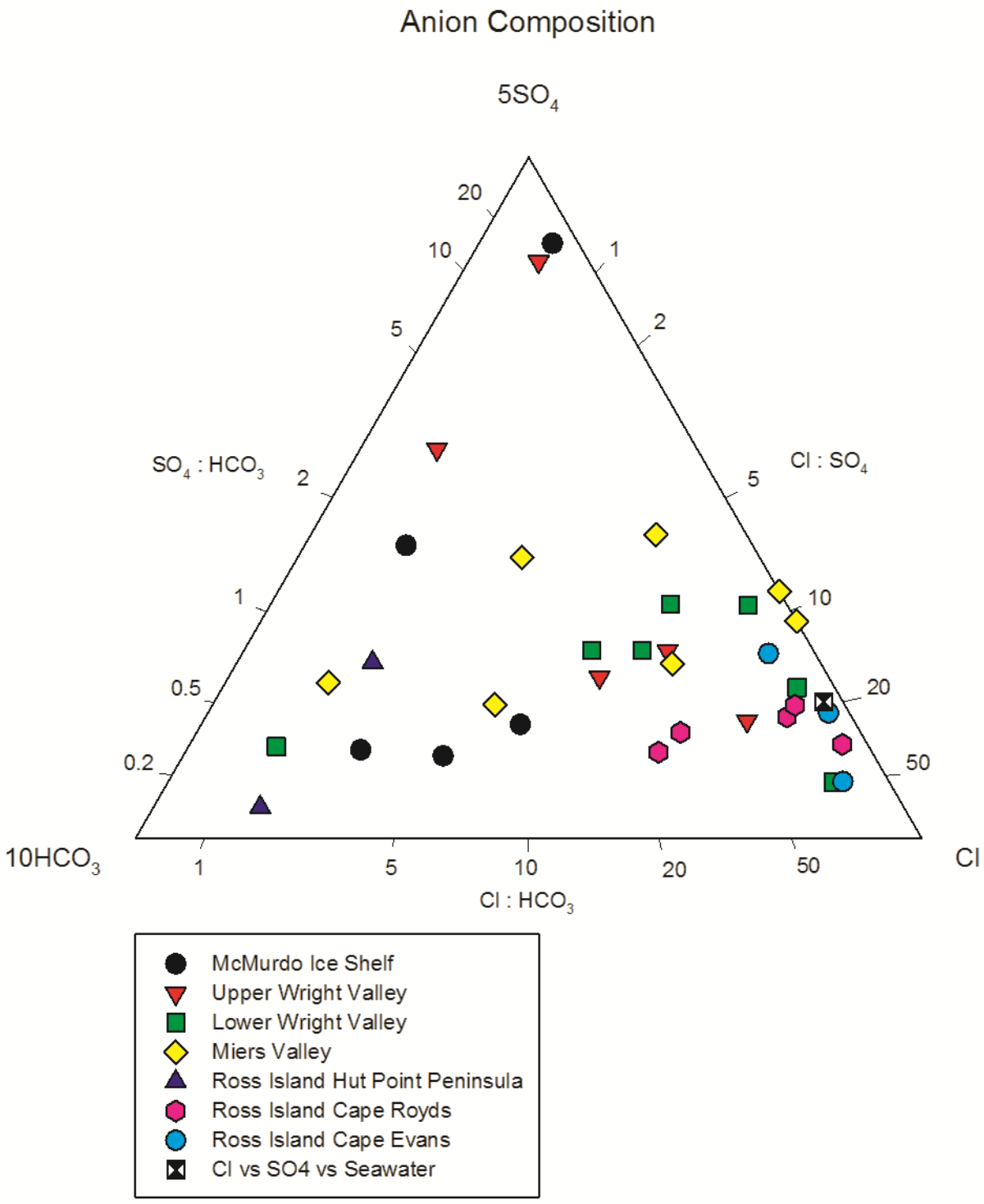


Fig. 6.15 Molar anion composition of pond waters at each sample site, as well as standard seawater for comparison (Millero *et al.* 2008).

Anion composition varied more widely between ponds at each site than the cation composition (Fig. 6.15). Most ponds were dominated by Cl^-, however in one study pond at each of Bratina Island and the Upper Wright Valley SO_4^{2-} was the dominant anion. The ponds at Cape Royds and Cape Evans on Ross Island had similar anionic composition to seawater, while those at Hut Point Peninsula were more HCO_3^- rich. The study ponds at the other sample sites had a wide range of anionic compositions. Major ion chemistry in ponds results from a combination of seawater (in coastal systems), atmospherically derived salts, catchment weathering processes, and freezing and evaporation cycles (Torii *et al.* 1989, Takamatsu *et al.* 1998, Wait 2011). No correlation was observed between water column P concentrations and conductivity, or the concentration of any major ion (Appendix 4).

Sediments appear to be the major source of P to ponds over time, which means that the ultimate factor limiting pond P chemistry is the soil, from which sediment P composition is derived. Therefore, it seems that the influence of location on the observed inorganic N:P ratios is a product of both the soil composition, which is derived from bedrock weathering and till deposits, together with nitrogen contributed largely from atmospheric sources (Campbell & Claridge 1987, Vincent & Howard-Williams 1994). Subsequent biological demand may then alter the N:P ratio through uptake particular to an organisms stoichiometric requirements (Stumm & Morgan 1996).

The soluble P in soils will be the first to become available after the soil is inundated. Soil transects from ponds at Bratina Island and the Miers Valley support loss of soluble and reactive P fractions from soils proximal to ponds. Apatite P is the major fraction in soils and sediments, and is generally considered to be non-bioavailable to aquatic systems (Psenner *et al.* 1988). This study shows that pond sediments have significantly reduced apatite P concentrations relative to nearby soils, and the sediment cores in the Upper Wright Valley revealed that surface sediments had 40 % lower apatite P concentrations near the sediment surface than at 6 to 8 cm depth. This strongly indicates that apatite P is being weathered in the sediments and made available to the pond.

There was a correlation between the log transformed total P concentration in soils and elevation (R^2 = 0.87, Fig. 6.16). This indicates there may be some factor that changes with elevation that also influences soil P concentrations. Ultimately, the rock or sediments from which soils are derived will ultimately determine the soil P concentration. Bate *et al.* (2008) established the

influence of landscape history on soil P composition via glacial tills. The location and elevation of a site can impact the glacial deposits at that site. The observed pattern may be a combination of local bedrock and elevation effects. The Labyrinth is the highest elevation site studied for this work, and soils are principally derived from disintegration of the dolerite bedrock (Campbell & Claridge 1987). The soil P content here is likely constrained by P present in the dolerite, and subsequent leaching during the wet formation processes of the feature, and historic pond levels. The remaining sample sites are less than 300 m above sea level, and the Miers, Lower Wright and McMurdo Ice Shelf all contain drift deposited by advancement of grounded ice from the Ross Sea Embayment during the last glacial maximum (Denton & Marchant 2000, Hall & Denton 2005).

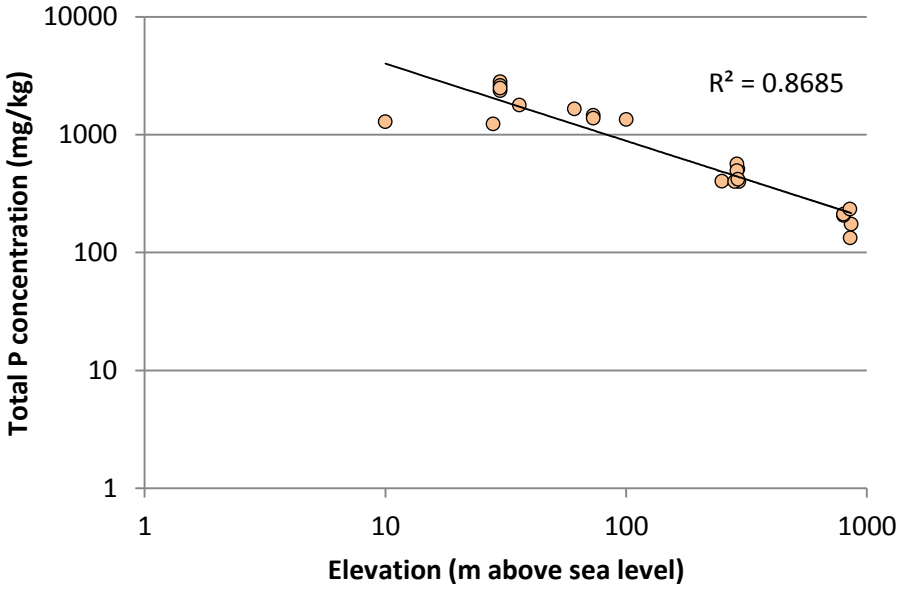


Fig. 6.16 Graph of pond elevation versus the total P concentration in soil near the pond edge

Marine sediments are typically rich in P, though characterization of the Ross Sea sediment P chemistry has not been published to date (Filippelli 1997). If the grounded ice from the Ross Embayment deposited marine derived drift to the sample sites, it is likely that the lower elevation sites will have relatively more marine material than higher elevation sites, which will contain a greater proportion of terrestrial and local drift (Goudie 2004). The debris on the McMurdo Ice Shelf is also comprised of marine sediments and faunal remains transported to the surface via ablation (Glasser *et al.* 2006). Kenyte erratics from Ross Island in the Miers Valley suggest that

the grounded ice flowed south and west, and it is likely the deposits in the Lower Wright Valley are of different origin to those deposited in the Miers Valley mouth (Denton & Marchant 2000). In the Lower Wright Valley coastal drift from the LGM advance may also be mixed with debris from within the valley, derived from the marbles, hornfelses and schists that comprise the valley bedrock (McKelvey & Webb 1962).

The Ross Island soils are derived from the alkaline basalts that make up the island. It is likely that a coastal site situated on P deficient sand stone would have low total P in the soils, while an inland site on an alkaline basalt volcano may have soil P concentrations similar to those measured on Ross Island. The nature of this elevation – phosphorus concentration relationship may be further revealed by visiting different locations, particularly more than one location that is more than 50 km from the coast.

6.6 Summary

This chapter determined several factors regulating water column P concentrations in ponds, and assessed the similarities and differences in P biogeochemistry observed at and between the sample sites studied in this thesis.

Key findings:

- Rapid changes in DRP concentrations occur in meltwater ponds that are not closely linked to the physico-chemical changes that take place in a diurnal cycle.
- The microbial mat in ponds is the major sink of DRP from the water column, however in some ponds phytoplankton are also a significant consumer of water column P
- Respiration releases significant DRP to the water column, and low light may cause a seasonal pulse of DRP to the water as the pond freezes in winter.
- Sediments are the major P source to melt water ponds in Victoria Land, Antarctica.
- Location influences P abundance, and this is likely due to local soil P composition.
- Log transformed ratios of inorganic N:P in the water column of ponds are correlated with elevation, as are soil total P concentrations.

Chapter 7:
Conclusions

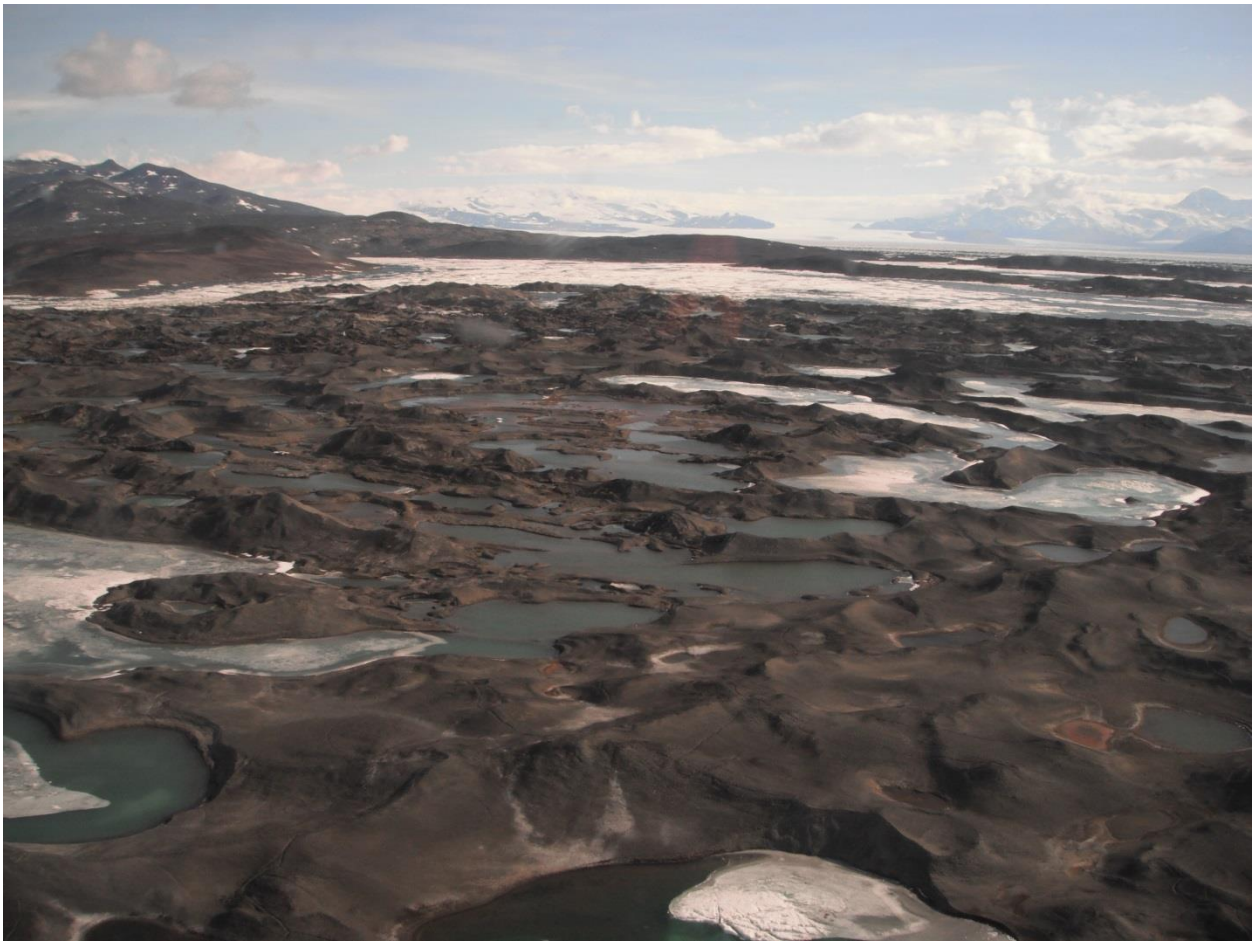


Fig 7.1 Meltwater ponds of the McMurdo Ice Shelf in January 2011. Brown Peninsula, the Blue Galcier, and the Royal Society Range are visible in the background from right to left.

7.1 Summary of thesis

This thesis characterizes phosphorus biogeochemistry in meltwater ponds at 7 sites in Victoria Land, and underscores both the importance of sediments as a P source to ponds, and the influence of location on P abundance.

P distribution at coastal ponds of the McMurdo Ice Shelf was characterized in Chapter 3. The four main reservoirs identified as important to P cycling in ponds were the pond water, microbial mat, sediment and soil. A conceptual model for phosphorus distribution in coastal ponds showed that sediments are the major reservoir for P in meltwater ponds, and also the main P source. The role of intermittent P sources was also investigated by analyzing the labile P concentrations in aerially transported dust, and the impact of skua guano on soil labile P concentrations. Sediments had significantly lower P concentrations than the soils, indicating substantial loss of P to the pond over time.

A similar analysis of P distribution was performed on inland ponds of the Labyrinth in the Upper Wright Valley (Chapter 4). The conceptual model for phosphorus distribution in inland ponds is similar to that of coastal ponds, although the relative P content of the microbial mat was found to be typically higher in the inland pools. Sediments and soils contain similar concentrations of total P, however concentrations were approximately 30 % lower than those of other Dry Valley soils developed on similar bedrock geologies. The soils close to the ponds are likely to be desiccated sediments, which have acted as a P source to ponds when inundated.

Phosphorus distribution in a number of coastal and intermediate meltwater systems was consistent with the models constructed in the previous chapters (Chapter 5). The abundance of P was greatest at coastal sites, and lowest in inland areas, however regardless of location the distribution of P in the pond reservoirs was similar. The concentration of total P in pond sediments was consistently only 50 to 80 % of the total P concentration in soils, indicating the importance of sediments as a P source to ponds via weathering of apatite P.

Processes that may affect P distribution in ponds were investigated in Chapter 6. Rapid changes in DRP concentrations occurred that were seemingly unrelated to changing physico-chemical parameters during diurnal cycles. Benthic mats played an important role in biological uptake of P in nutrient amended microcosms, and respiration of benthic mats in dark conditions caused DRP

release to the water column. Location did not appear to alter rates of nutrient uptake, however location had a strong impact on P abundance in pond reservoirs.

7.2 Outcomes

The major objective of this PhD research was to establish the major components of the phosphorus cycle in meltwater ponds of Victoria Land. A complete P cycle has not been proposed from this work, however four demonstrable outcomes have allowed some of the major components of the P cycle to be identified for most meltwater systems in the region (Fig 7.2).

7.2.1 Distribution of P in meltwater ponds

Four key reservoirs of P are important to P dynamics within the 35 ponds studied. Modelling reveals that distribution of P between these reservoirs is very similar at all sample sites (Fig. 7.2). The sediment is the major reservoir of P for nearly all meltwater ponds, and generally contains more than 60 % of the total P present in the pond ecosystem. Saturated soils surrounding the pond are also a key P reservoir, and contain most of the remaining P. Benthic microbial mats and the water column of ponds contain < 0.1 % of a pond's total P. The vast majority of P in meltwater ponds is tied up in the apatite P fractions of the soils and sediments.

7.2.2 Sources of P to meltwater ponds

The major source of P to meltwater ponds identified in this thesis is the pond sediments (Fig 7.2). At nearly every pond sampled, the total P concentration in the sediment was significantly lower than the total P concentration in soils close to the pond edge. This demonstrates that over time sediment P is being transported into the microbial mat and pond water. Immediately adjacent soils also contribute P to the ponds, as demonstrated by decreased concentrations of some of the reactive and apatite P fractions in soils 0-2 m from the pond shorelines. Dust and seabird guano are also intermittent sources of P to ponds, and provide high concentrations of labile P relative to soils. In this work it was not possible to rigorously determine the rates at which dust and guano may be supplied to ponds. There is a need to address this to provide a comprehensive model of the P cycle in meltwater ponds.

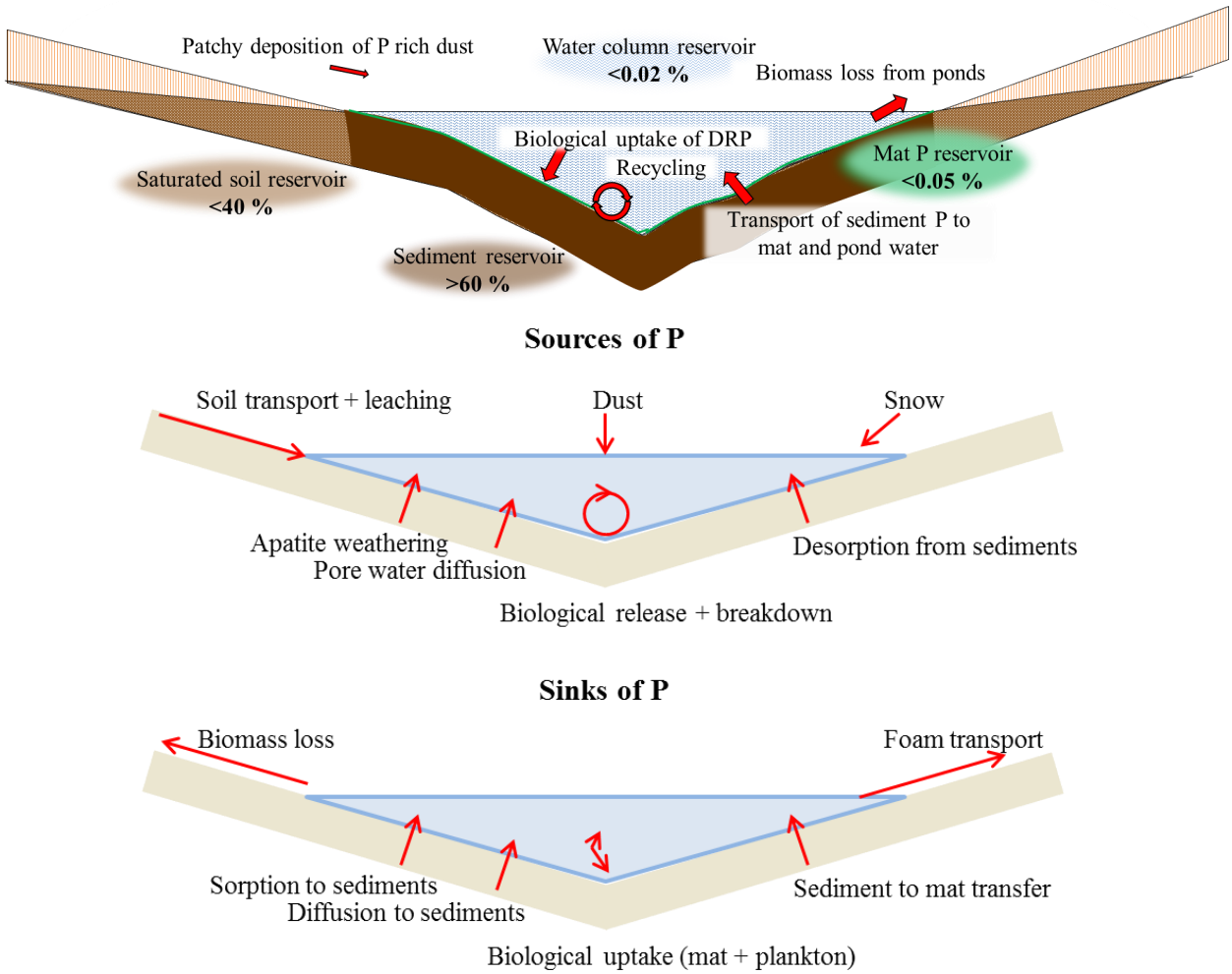


Fig. 7.2 Summary of the major components of the P cycle in meltwater ponds

a) Showing the main P reservoirs and their relative P content in most ponds, with red arrows depicting some of the key transfer processes that were documented in this study.
b) Key processes which contribute P to ponds as measured and indicated in this study
c) Key processes which remove P from ponds as measured and indicated in this study

7.2.3 Processes affecting P in meltwater ponds

There is a strong biotic control on water column P concentrations, evidenced by changes in water DRP concentration when conditions were manipulated. Microbial mats are the principal consumer of water column DRP in most ponds, and remove DRP from the water column when photosynthetically active (Fig 7.2). In dark conditions, mats contribute DRP to pond water through respiration. Daily fluctuations in physico-chemical parameters appear to have little effect

on pond DRP concentration, although short term fluctuations in DRP concentration do occur and are likely to be a result of biological turnover.

7.2.4 Influence of location on P dynamics

The location of a meltwater pond has a large influence on the abundance of P in the pond. Log transformed water column N:P ratios, and soil total P concentrations correlate with pond elevation above sea level. Landscape history and drift composition influence P concentrations in soils, which ultimately form pond sediments via inundation or transport and accumulation in a pond. The soil P correlation with elevation may be partially caused by drift left by the advance of grounded ice in the Ross Embayment in the last glacial maximum, perhaps depositing a greater proportion of P rich marine sediment at lower elevations. However, the concentrations at Ross Island and the Upper Wright Valley are a result of local geology and subsequent landscape history, with soils derived from local bedrock rather than tills. As pond P is sourced from sediments, concentrations of P in soils helps determine the P concentrations in other reservoirs of meltwater ponds.

7.3 Further research

This research highlights a number of opportunities that would enhance knowledge of meltwater ponds, and their phosphorus cycle.

This thesis has established the important reservoirs of phosphorus in meltwater ponds, and highlighted sediments as a major P source to ponds over time. An attempt to measure P flux from the water column to the microbial mat was made with relative success, but further fluxes for the phosphorus cycle in meltwater systems were not determined. The conceptual model of major processes that transfer P to, from, and within meltwater ponds makes a start on proposing a P cycle for meltwater ponds. Establishing the rates of transfer over an annual or decadal timescale would allow a complete model of the P cycle to be constructed for these ecosystems. A useful study could involve investigating P flux between the key reservoirs, and the also the major P species. This could be performed using a series of field and lab experiments. Key areas to target would be internal exchange of sediment P with the mat and pond water, recycling of P species by biota, and external P sources and sinks via soil leaching, dust, and foam and biomass loss.

Detailed understanding of organic phosphorus, and its importance to the phosphorus cycle in aquatic systems is becoming increasingly apparent (Turner *et al.* 2005). The metal oxide and organic P fraction extracted in NaOH for the sequential extractions used in this thesis target phosphate adsorbed to metal oxides as well as acidic organic phosphorus compounds. Numerous research groups have utilized ^{31}P NMR to probe the coordination chemistry of P in NaOH extracts from sediments, which enables identification of the functional group with which P atoms in the sample are associated (Reitzel *et al.* 2007, Ozkundakci *et al.* 2014). This technique was trialed on both Antarctic and temperate sediments, as well as microbial mat samples to enable organic P speciation to be reported in this thesis. There was limited success on the microbial mat sample extract, with some organic P functional groups detected, however only DRP and a small signal indicating pyrophosphate could be determined in sediment extracts. This method would be worth pursuing as it would enable the potential bioavailability of organic P present in the sediments to be assessed, both by reactivity and a comparison of DOP species in the mat versus the soil would indicate which species are readily broken down during respiration and decomposition. Some ponds such as Salt are capable of accumulating very high DOP concentrations, and better understanding the role of organic P in meltwater pond P cycles may indicate why this occurs only at some sample sites.

Finally, during freeze-thaw cycles, the physical and chemical changes that occur in ponds are likely to significantly influence P chemistry. The FREZCHEM62 geochemical model has been validated for application in Antarctic ponds, and accurately predicts water and precipitate compositions as ponds freeze (Healy *et al.* 2006, Wait 2011). It is anticipated that freeze-thaw cycles may promote weathering of apatite P in the sediments, and also facilitate exchange from the mat to the water column. A combination of lab based experiments together with geochemical modelling may provide insight into any seasonal changes in P dynamics in meltwater ponds.

7.4 Final thoughts

Phosphorus is a key nutrient to aquatic systems worldwide. The results presented in this thesis add to the current understanding of biogeochemistry in Victoria Land meltwater ponds. Ponds from a variety of locations, with different nutrient and major ion chemistries showed remarkably consistent P distribution. There are broad similarities between ponds in Victoria Land, and other locations in Antarctica, and it is likely that the models put forward for Victoria Land ponds will

predict distribution and key processes in other areas. In temperate aquatic systems, the increased complexity in hydrology and trophic levels will result in a greater diversity of P distribution; however key processes affecting P chemistry are likely to be similar.

Meltwater ponds are important biodiversity elements in Antarctica, hosting high concentrations of biomass in their benthic and planktonic habitats. The ponds are closely linked to climate, typically relying on weather events depositing water sources into their catchments. One of the motivations for this research was to improve understanding of phosphorus sources and availability in meltwater ponds, in order to provide some insight into potential responses of meltwater ponds to changes in climate. Any climatic effect on meltwater availability is not in the scope of this work, however if meltwater volumes increase habitat sizes, there is potential for some changes in phosphorus availability. An increased habitat size would inundate more soil, and in coastal areas this would be likely to cause an increase in pond phosphorus concentrations. In inland systems however, there is little soluble and reactive P available to be dissolved in soils. The apatite P fractions in inundated soils might be expected to weather at a similar rate to that in the existing sediments, and it is unlikely that the P limited nutrient status would change.

References

AISLABIE, J., NOVIS, P. & FERRARI, B. 2014. Microbiology of Eutrophic (Ornithogenic and Hydrocarbon-Contaminated) Soil. *In* Cowan, D.A., *ed. Antarctic Terrestrial Microbiology.* Springer Berlin Heidelberg, 91-113.

ARCHER, S.D.J., MCDONALD, I.R., HERBOLD, C.W. & CARY, S.C. 2014. Characterisation of bacterioplankton communities in the meltwater ponds of Bratina Island, Victoria Land, Antarctica. *Fems Microbiology Ecology,* **89**, 451-464.

ATKINS, P. & PAULA, J.D. 2006. *Atkins' Physical Chemistry*, 8 ed. Oxford: Oxford University Press,

BATE, D.B., BARRETT, J.E., POAGE, M.A. & VIRGINIA, R.A. 2008. Soil phosphorus cycling in an Antarctic polar desert. *Geoderma,* **144**, 21-31.

BELL, E.M. & LAYBOURN-PARRY, J. 1999. Annual plankton dynamics in an Antarctic saline lake. *Freshwater Biology,* **41**, 507-519.

BENGTSSON, A. & SJOBERG, S. 2009. Surface complexation and proton-promoted dissolution in aqueous apatite systems. *Pure and Applied Chemistry,* **81**, 1569-1584.

BERNER, K.B. & BERNER, R.A. 1996. *Global Environment Water, Air and Geochemical Cycles*. New Jersey: Prentice-Hall, Inc.,

BLANK, H., WHEELER, R., RH, C. & WILLIS, I. 1963. Geology of the Koettlitz - Blue Glacier region, S. Victoria Land, Antarctica. *Transactions of the Royal Society of New Zealand, Geology,* **2**, 79-100.

BLECKER, S.W., IPPOLITO, J.A., BARRETT, J.E., WALL, D.H., VIRGINIA, R.A. & NORVELL, K.L. 2006. Phosphorus fractions in soils of Taylor Valley, Antarctica. *Soil Science Society of America Journal,* **70**, 806-815.

BOCKHEIM, J.G. & MCLEOD, M. 2006. Soil formation in Wright Valley, Antarctica since the Late Neogene. *Geoderma,* **137**, 109-116.

BOMBLIES, A., MCKNIGHT, D.M. & ANDREWS, E.D. 2001. Retrospective simulation of lake-level rise in Lake Bonney based on recent 21-year record: indication of recent climate change in the McMurdo Dry Valleys, Antarctica. *Journal of Paleolimnology,* **25**, 477-492.

BROADY, P.A. 1989. Broadscale patterns in the distribution of aquatic and terrestrial vegetation at 3 ice-free regions on Ross Island, Antarctica. *Hydrobiologia,* **172**, 77-95.

CAMPBELL, I.B. & CLARIDGE, G.G.C. 1987. *Antarctica: Soils, Weathering Processes and Environment*. Amsterdam: Elsevier,

CLAYTON-GREENE, J., HENDY, C. & HOGG, A. 1988. Chronology of a Wisconsin age proglacial lake in the Miers Valley, Antarctica. *New Zealand Journal of Geology and Geophysics,* **31**, 353-361.

COLMAN, S.M. & DETHIER, D.P., *eds.* 1986. *Rates of chemical weathering of rocks and minerals*. Orlando: Academic Press,

CORNELL, R. & SCHWERTMANN, U. 2003. *The Iron Oxides: Structure, Properties, Reactions, Occurences and Uses*, 2 ed. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA,

CORNELL, R.M. & SCHWERTMANN, U. 2006. *The iron oxides: structure, properties, reactions, occurrences and uses*. John Wiley & Sons,

DAVID, T.W.E., PRIESTLEY, R.E., TAYLOR, T.G. & GODDARD, E. 1914. *Glaciology, physiography, stratigraphy, and tectonic geology of South Victoria Land*. William Heinemann,

DEMORA, S.J., WHITEHEAD, R.F. & GREGORY, M. 1994. The chemical composition of glacial melt water ponds and streams on the McMurdo Ice Shelf, Antarctica. *Antarctic Science,* **6**, 17-27.

DENTON, G.H. & MARCHANT, D.R. 2000. The geologic basis for a reconstruction of a grounded ice sheet in McMurdo Sound, Antarctica, at the last glacial maximum. *Geografiska Annaler: Series A, Physical Geography,* **82**, 167-211.

DORE, J.E. & PRISCU, J.C. 2001. Phytoplankton phosphorus deficiency and alkaline phosphatase activity in the McMurdo Dry Valley lakes, Antarctica. *Limnology and Oceanography,* **46**, 1331-1346.
EICHEL, K.A., MACRAE, M.L., HALL, R.I., FISHBACK, L. & WOLFE, B.B. 2014. Nutrient Uptake and Short-Term Responses of Phytoplankton and Benthic Algal Communities from a Subarctic Pond to Experimental Nutrient Enrichment in Microcosms. *Arctic Antarctic and Alpine Research,* **46**, 191-205.
FILIPPELLI, G.M. 1997. Controls on phosphorus concentration and accumulation in oceanic sediments. *Marine Geology,* **139**, 231-240.
FOX, A.J. & COOPER, P.R. 1994. Measured properties of the Antarctic Ice Sheet derived from the SCAR digital database. *Polar Record,* **30**, 201-204.
GLASSER, N.F., GOODSELL, B., COPLAND, L. & LAWSON, W. 2006. Debris characteristics and ice-shelf dynamics in the ablation region of the McMurdo Ice Shelf, Antarctica. *Journal of Glaciology,* **52**, 223-234.
GOUDIE, A. 2004. *Encyclopedia of geomorphology*. Psychology Press,
HALL, B.L. & DENTON, G.H. 2005. Surficial geology and geomorphology of eastern and central Wright Valley, Antarctica. *Geomorphology,* **64**, 25-65.
HANSSON, L.A. 1988. Effects of competitive interactions on the biomass development of planktonic and periphytic algae in lakes. *Limnology and Oceanography,* **33**, 121-128.
HAWES, I., HOWARDWILLIAMS, C. & PRIDMORE, R.D. 1993. Environmental-control of microbial biomass in the ponds of the McMurdo Ice Shelf, Antarctica. *Archiv für Hydrobiologie,* **127**, 271-287.
HAWES, I. & HOWARD-WILLIAMS, C. 1998. Primary production processes in streams of the McMurdo Dry Valleys, Antarctica. *In* Priscu, J.C., *ed. Ecosystem Dynamics in a Polar Desert: the Mcmurdo Dry Valleys, Antarctica.* Washington, D. C.: American Geophysical Union,
HAWES, I., SUMNER, D.Y., ANDERSEN, D.T. & MACKEY, T.J. 2011. Legacies of recent environmental change in the benthic communities of Lake Joyce, a perennially ice-covered Antarctic lake. *Geobiology,* **9**, 394-410.
HAWES, I., HOWARD-WILLIAMS, C. & SORRELL, B. 2014. Decadal timescale variability in ecosystem properties in the ponds of the McMurdo Ice Shelf, southern Victoria Land, Antarctica. *Antarctic Science,* **26**, 219-230.
HEALY, M., WEBSTER-BROWN, J.G., BROWN, K.L. & LANE, V. 2006. Chemistry and stratification of Antarctic meltwater ponds II: Inland ponds in the McMurdo Dry Valleys, Victoria Land. *Antarctic Science,* **18**, 525-533.
HEDLEY, M.J., STEWART, J.W.B. & CHAUHAN, B.S. 1982. Changes in Inorganic and Organic Soil Phosphorus Fractions Induced by Cultivation Practises and by Laboratory Incubations. *Soil Science Society of America Journal,* **46**, 970-976.
HESSE, P.R. 1973. Phosphorus in Lake Sediments. *In* Griffith, E.J., Beeton, A., Spencer, J.M. & Mitchel, D.T., *eds. Environmental phosphorus handbook.* New York: John Wiley and Sons,
HOWARD-WILLIAMS, C., PRIDMORE, R., DOWNES, M.T. & VINCENT, W.F. 1989. Microbial biomass, photosynthesis and chlorophyll a related pigments in the ponds of the McMurdo Ice Shelf, Antarctica. *Antarctic Science,* **1**, 125-131.
HOWARD-WILLIAMS, C., PRIDMORE, R.D., BROADY, P.A. & VINCENT, W.F. 1990. Environmental and Biological Variability in the McMurdo Ice Shelf Ecosystem. *In* K. R. Kerry, G.H., *ed. Antarctic Ecosystems: Ecological Change and Conservation.* Germany: Springer-Verlag, 23-31.
HOWARD-WILLIAMS, C., HAWES, I., SCHWARZ, A.-M. & HALL, J.A. 1997. Sources and sinks of nurients in a polar desert stream, the Onyx River, Antarctica. *In* W.B. Lyons, C.H.-W., I. Hawes, *ed. Ecosystem Processes in Antarctic Ice-free Landscapes.* Netherlands: A.A. Balkema,
KAUP, E. & BURGESS, J.S. 2002. Surface and subsurface flows of nutrients in natural and human impacted lake catchments on Broknes, Larsemann Hills, Antarctica. *Antarctic Science,* **14**, 343-352.
KAWASHIMA, M., TAINAKA, Y., HORI, T., KOYAMA, M. & TAKAMATSU, T. 1986. Phosphate adsorption onto hydrous manganese (IV) oxide in the presence of divalent cations. *Water research,* **20**, 471-475.

KYLE, P. & COLE, J. 1974. Structural control of volcanism in the McMurdo Volcanic Group, Antarctica. *Bulletin Volcanologique,* **38**, 16-25.
KYLE, P. & TREVES, S. 1974. Geology of Hut Point Peninsula, Ross Island. *Antarctic Journal of the United States,* **9**, 232-234.
LAJTHA, K., DRISCOLL, C.T., JARRELL, W.M. & ELLIOTT, E.T. 1999. Soil Phosphorus: Characterisation and Total Element Analysis. *In* Robertson, G.P., Coleman, D.C., Bledsoe, C.S. & Sollins, P., *eds. Standard Soil Methods for Long-Term Ecological Research.* Oxford: Oxford Univeristy Press,
LANOIL, B., SKIDMORE, M., PRISCU, J.C., HAN, S., FOO, W., VOGEL, S.W., TULACZYK, S. & ENGELHARDT, H. 2009. Bacteria beneath the West Antarctic Ice Sheet. *Environmental Microbiology,* **11**, 609-615.
LEVINE, M.A. & WHALEN, S.C. 2001. Nutrient limitation of phytoplankton production in Alaskan Arctic foothill lakes. *Hydrobiologia,* **455**, 189-201.
LEWIS, A.R., MARCHANT, D.R., KOWALEWSKI, D.E., BALDWIN, S.L. & WEBB, L.E. 2006. The age and origin of the Labyrinth, western Dry Valleys, Antarctica: Evidence for extensive middle Miocene subglacial floods and freshwater discharge to the Southern Ocean. *Geology,* **34**, 513-516.
LYON, G.L. 1978. The stable isotope geochemistry of gypsum, Miers Valley, Antarctica. *Stable isotopes in the earth sciences.*
LYONS, W.B., WELCH, K.A., NEZAT, C.A., CRICK, K., TOXEY, J.K., MASTRINE, J.A. & MCKNIGHT, D.M. 1997. Chemical weathering rates and reactions in the Lake Fryxell Basin, Taylor Valley: Comparison to temperate river basins. *In* Lyons, W.B., HowardWilliams, C. & Hawes, I., *eds. Ecosystem Processes in Antarctic Ice-Free Landscapes.* 147-154.
LYONS, W.B. & FINLAY, J.C. 2008. Biogeochemical processes in high-latitude lakes and rivers. *In* Vincent, W.F. & Laybourn-Parry, J., *eds. Polar Lakes and Rivers: Limnology of Arctic and Antarctic Aquatic Ecosystems.* Oxford: Oxford University Press,
MCKELVEY, B. & WEBB, P. 1962. Geological investigations in Southern Victoria Land, Antarctica: part 3—Geology of Wright Valley. *New Zealand Journal of Geology and Geophysics,* **5**, 143-162.
MCLEOD, M., BOCKHEIM, J., BALKS, M. & AISLABIE, J. 2009. Soils of western Wright Valley, Antarctica. *Antarctic Science,* **21**, 355-365.
MILLERO, F.J., FEISTEL, R., WRIGHT, D.G. & MCDOUGALL, T.J. 2008. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep Sea research Part I: oceanographic research papers,* **55**, 50-72.
MOORHEAD, D.L., BARRETT, J.E., VIRGINIA, R.A., WALL, D.H. & PORAZINSKA, D. 2003. Organic matter and soil biota of upland wetlands in Taylor Valley, Antarctica. *Polar Biology,* **26**, 567-576.
MOUNTFORT, D.O., KASPAR, H.F., ASHER, R.A. & SUTHERLAND, D. 2003. Influences of pond geochemistry, temperature, and freeze-thaw on terminal anaerobic processes occurring in sediments of six ponds of the McMurdo Ice Shelf, near Bratina Island, Antarctica. *Applied and Environmental Microbiology,* **69**, 583-592.
MURRAY, J. 2011. On collecting at Cape Royds. *In* Graham, M.H., Parker, J. & Dayton, P.K., *eds. The Essential Naturalist: Timeless Readings in Natural History.* Chicago and London: University of Chicago Press, 148-157.
OZKUNDAKCI, D., HAMILTON, D.P., MCDOWELL, R. & HILL, S. 2014. Phosphorus dynamics in sediments of a eutrophic lake derived from P-31 nuclear magnetic resonance spectroscopy. *Marine and Freshwater Research,* **65**, 70-80.
PRISCU, J.C. & FOREMAN, C.M. 2009. Lakes of Antarctica. *In* Likens, G.E., *ed. Encyclopedia of Inland Waters.* Oxford: Academic Press, 555-566.
PSENNER, R., BOSTRÖM, B., DINKA, M., PETTERSSON, K., PUCSKO, R. & SAGER, M. 1988. Fractionation of phosphorus in suspended matter and sediment. *Arch. Hydrobiol. Beih. Ergebn. Limnol,* **30**, 98-103.
REDFIELD, A.C. 1958. The biological control of chemical factors in the environment. *American Scientist,* **46**, 205-221.

REITZEL, K., AHLGREN, J., DEBRABANDERE, H., WALDEBÄCK, M., GOGOLL, A., TRANVIK, L. & RYDIN, E. 2007. Degradation rates of organic phosphorus in lake sediment. *Biogeochemistry,* **82**, 15-28.

RIGLER, F. 1973. A dynamic view of the phosphorus cycle in lakes. *Environmental phosphorus handbook,* 539-572.

RUBAN, V., LOPEZ-SANCHEZ, J.F., PARDO, P., RAURET, G., MUNTAU, H. & QUEVAUVILLER, P. 1999. Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment. *Journal of Environmental Monitoring,* **1**, 51-56.

RYDIN, E. 2000. Potentially mobile phosphorus in Lake Erken sediment. *Water Research,* **34**, 2037-2042.

SCHMIDT, S., MOSKAL, W., DEMORA, S.J., HOWARDWILLIAMS, C. & VINCENT, W.F. 1991. LIMNOLOGICAL PROPERTIES OF ANTARCTIC PONDS DURING WINTER FREEZING. *Antarctic Science,* **3**, 379-388.

SHAW, J. & HEALY, T.R. 1977. Formation of Labyrinth, Wright Valley, Antarctica. *New Zealand Journal of Geology and Geophysics,* **20**, 933-947.

SORRELL, B.K., HAWES, I. & SAFI, K. 2013. Nitrogen and carbon limitation of planktonic primary production and phytoplankton-bacterioplankton coupling in ponds on the McMurdo Ice Shelf, Antarctica. *Environmental Research Letters,* **8**, 10.

STANISH, L.F., BAGSHAW, E.A., MCKNIGHT, D.M., FOUNTAIN, A.G. & TRANTER, M. 2013. Environmental factors influencing diatom communities in Antarctic cryoconite holes. *Environmental Research Letters,* **8**, 8.

STERNER, R.W., ANDERSEN, T., ELSER, J.J., HESSEN, D.O., HOOD, J.M., MCCAULEY, E. & URABE, J. 2008. Scale-dependent carbon : nitrogen : phosphorus seston stoichiometry in marine and freshwaters. *Limnology and Oceanography,* **53**, 1169-1180.

STUMM, W. & MORGAN, J.J. 1996. *Aquatic chemistry: chemical equilibria and rates in natural waters*, 3 ed. United States of America: John Wiley & Sons,

TAKAMATSU, N., KATO, N., MATSUMOTO, G.I. & TORII, T. 1998. The origin of salts in water bodies of the McMurdo Dry Valleys. *Antarctic Science,* **10**, 439-448.

TORII, T., MATSUMOTO, G.I. & NAKAYA, S. 1988. The Chemical Characteristics of Antarctic Lakes and Ponds, with Special Emphasis on the Distribution of Nutrients. *Polarforschung,* **58**, 219-230.

TORII, T., NAKAYA, S., MATSUBAYA, O., MATSUMOTO, G.I., MASUDA, N., KAWANO, T. & MURAYAMA, H. 1989. Chemical characteristics of pond waters in the Labyrinth of Southern Victoria Land, Antarctica. *Hydrobiologia,* **172**, 255-264.

TREVES, S.B. 1962. The geology of Cape Evans and Cape Royds, Ross Island, Antarctica. *Antarctic Research: The Matthew Fontaine Maury Memorial Symposium.* Wiley Online Library, 40-46.

TURNER, B.L., FROSSARD, E. & BALDWIN, D.S. 2005. *Organic Phosphorus in the Environment*. CABI Pub.,

VINCENT, W. & VINCENT, C. 1982. Response to nutrient enrichment by the plankton of Antarctic coastal lakes and the inshore Ross Sea. *Polar Biology,* **1**, 159-165.

VINCENT, W., CASTENHOLZ, R., DOWNES, M. & HOWARD-WILLIAMS, C. 1993. Antarctic cyanobacteria - light, nutrients, and photosynthesis in the microbial mat environment. *Journal of Phycology,* **29**, 745-755.

VINCENT, W. & HOWARD-WILLIAMS, C. 1994. Nitrate-rich inland waters of the Ross Ice Shelf region, Antarctica. *Antarctic Science,* **6**, 339-346.

VINCENT, W.F. & HOWARD-WILLIAMS, C. 1986. Antarctic stream ecosystems: physiological ecology of a blue-green algal epilithon. *Freshwater Biology,* **16**, 219-233.

VINCENT, W.F. & LAYBOURN-PARRY, J., *eds.* 2008. *Polar Lakes and Rivers: Limnology of Arctic and Antarctic Aquatic Ecosystems*. Oxford: Oxford University Press,

WAIT, B.R., WEBSTER-BROWN, J.G., BROWN, K.L., HEALY, M. & HAWES, I. 2006. Chemistry and stratification of Antarctic meltwater ponds I: Coastal ponds near Bratina Island, McMurdo Ice Shelf. *Antarctic Science,* **18**, 515-524.

WAIT, B.R., NOKES, R. & WEBSTER-BROWN, J.G. 2009. Freeze-thaw dynamics and the implications for stratification and brine geochemistry in meltwater ponds on the McMurdo Ice Shelf, Antarctica. *Antarctic Science,* **21**, 243-254.

WAIT, B.R. 2011. *Seasonal Extremes in Meltwater Chemistry at Bratina Island (Antarctica): Physical and Biogeochemical Drivers of Compositional Change*. University of Canterbury.

WEAND, B.L., HOEHN, R.C. & PARKER, B.C. 1977. Nutrient fluxes in Lake Bonney - A meromictic Antarctic lake. *Archiv für Hydrobiologie,* **80**, 519-530.

WEBSTER-BROWN, J. & WEBSTER, K. 2007. Trace metals in cyanobacterial mats, phytoplankton and sediments of the Lake Vanda region, Antarctica. *Antarctic Science,* **19**, 311-319.

WEBSTER-BROWN, J., HAWES, I., SAFI, K., SORRELL, B. & WILSON, N. 2012. Summer-winter transitions in Antarctic ponds: III. Chemical changes. *Antarctic Science,* **24**, 121-130.

WELCH, K.A., LYONS, W.B., WHISNER, C., GARDNER, C.B., GOOSEFF, M.N., MCKNIGHT, D.M. & PRISCU, J.C. 2010. Spatial variations in the geochemistry of glacial meltwater streams in the Taylor Valley, Antarctica. *Antarctic Science,* **22**, 662-672.

ZHU, R., MA, D., DING, W., BAI, B., LIU, Y. & SUN, J. 2011. Occurrence of matrix-bound phosphine in polar ornithogenic tundra ecosystems: Effects of alkaline phosphatase activity and environmental variables. *Science of The Total Environment,* **409**, 3789-3800.

Appendices

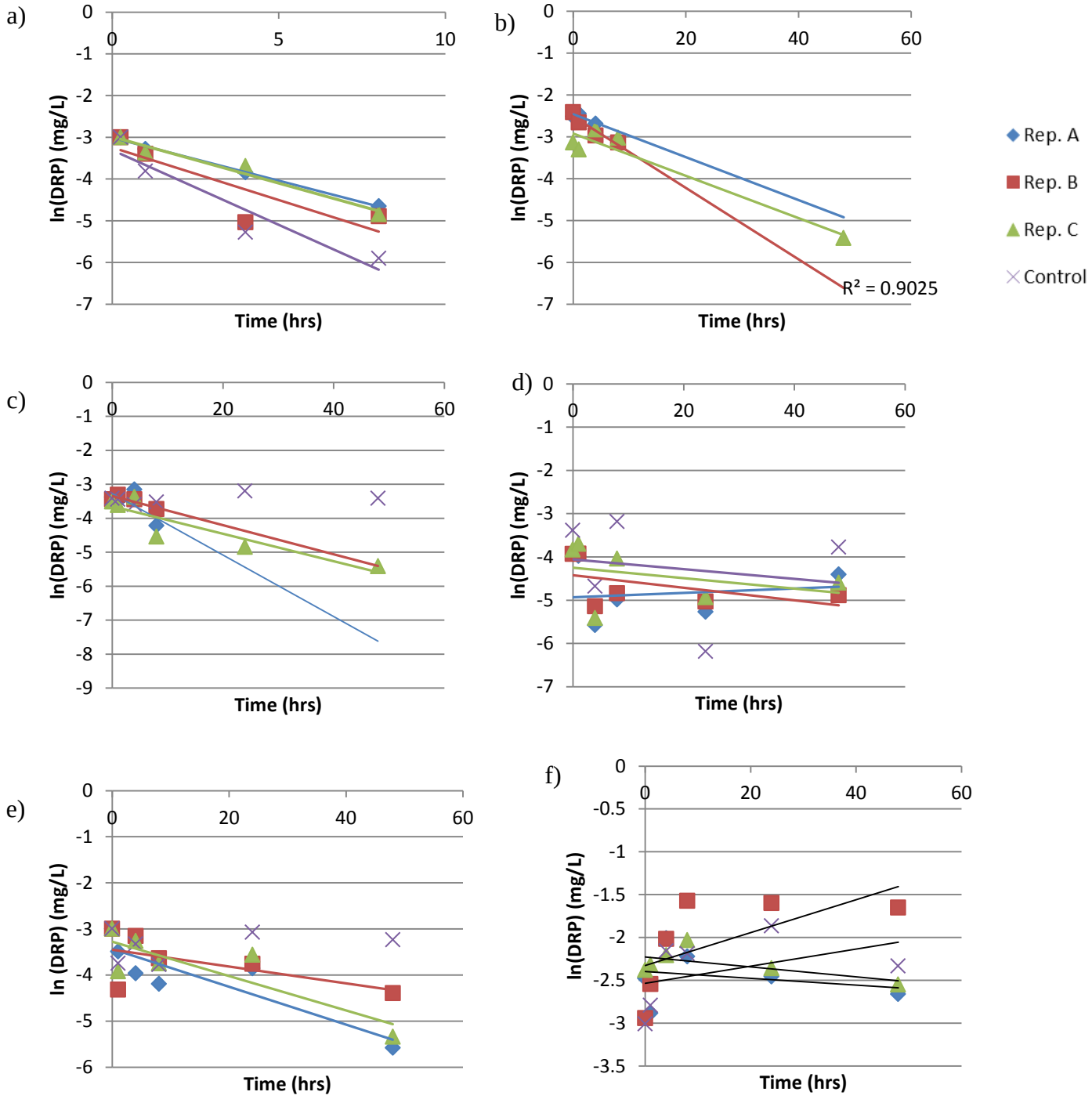
Appendix 1 – P data for additional ponds

Table A1. Summary of P concentrations and reservoir volumes and P content in ponds, including data from ponds that had incomplete sampling suites. na = not analysed.

	Pond length (m)	Pond breadth (m)	Depth (m)	Mat volume (m^3)	TP (mg/ m3)	DRP (mg/ m3)	DOP (mg/ m3)	PP (mg/ m3)	TP (g)	Mat biomass (kg/m2)	Mat P (mg/kg)	Mat P (kg)	Sediment vol (m3)	Sat. soil vol (m3)	Soil TP (mg/kg)	Soil reactive P (mg/kg)	Soil apatite P mg/kg	Soil TP kg
OHP	30	20	0.3	0.98	97.5	30	61.5	6	4.79	0.43	582	0.12	221	31	na	na	na	na
HP2	16	8	1	0.34	73.3	24	44.3	5	2.76	0.30	1386	0.05	52	18	1231	52	1180	44
LW2	30	20	0.6	0.49	9.7	0.5	4	5.2	0.95	0.89	423	0.09	221	31	402	8	393	25
LW12	24	22	1	0.43	20.9	0.5	11	9.4	2.89	0.64	965	0.13	188	29	401	4	396	23
LW13	20	8	1	0.16	14.8	0.5	4	10.3	0.76	0.66	2440	0.13	70	20	400	8	392	16
LW14	16	7	0.4	0.11	60.5	6.1	5.9	48.5	0.84	0.70	1710	0.07	47	17	510	12	498	18
LW15	15	12	0.5	0.16	16.4	2.3	2.9	11.2	0.39	1.05	1370	0.11	65	19	566	15	551	22
LW16	20	15	0.8	0.27	8.8	0.5	2	6.3	0.56	0.87	440	0.05	109	23	495	11	484	23
LW18	10	10	0.6	0.09	8.8	0.5	3	5.3	0.14	0.87	1570	0.06	36	16	418	4	414	13
Canary	9	7	1.05	0.06	179	59	56	64	3.15	1.93	1082	0.06	23	14	1653	38	1615	46
Macaw	12	8	1.5	0.10	55	16	8	31	2.16	1.21	1530	0.09	37	16	1785	40	1745	57
Robin	6	6	1.2	0.04	76	3	64	9	0.86	2.54	1065	0.05	14	12	na	na	na	na
Finch	8	6	0.4	0.05	99	4	68	27	0.51	2.86	988	0.07	17	13	na	na	na	na
Kingfisher	10	8	0.5	0.08	53	5	5	43	0.56	0.94	1428	0.05	29	15	na	na	na	na
Morepork	20	8	1.23	0.20	154	0.5	153	na	9.69	2.54	1069	0.27	70	20	na	na	na	na
Shackleton	85	25	1.5	3.09	80	2	66	12	95.03	0.44	2850	1.93	1071	60	1887	48	1410	227
Ernest	22	9	1	0.25	33	2	16	15	2.08	1.14	3300	0.47	86	21	na	na	na	na
Bart	17	10	0.5	0.19	54	3	32	19	1.29	0.89	400	0.03	65	19	1649	30	1350	64
Green Lake	70	40	1	3.23	166184	102	82	166,000	131608	1.79	1167	3.38	1070	60	na	na	na	na
Nimrod	7	6	1.75	0.05	82	33	12	37	1.59	0.92	1433	0.03	17	13	1783	56	1300	45
Pond 2	18	10	0.35	0.22	165	71	31	63	2.96	0.88	1750	0.17	69	20	1708	47	1240	68
Pond 3	18	9	0.4	0.21	98	16	26	56	1.87	1.42	2783	0.41	65	19	na	na	na	na

Appendix 2 – Uptake kinetics

Graphs of log transformed concentration of DRP over time in the microcosms that were spiked with 5 or 50 µg/L DRP in the uptake experiments.



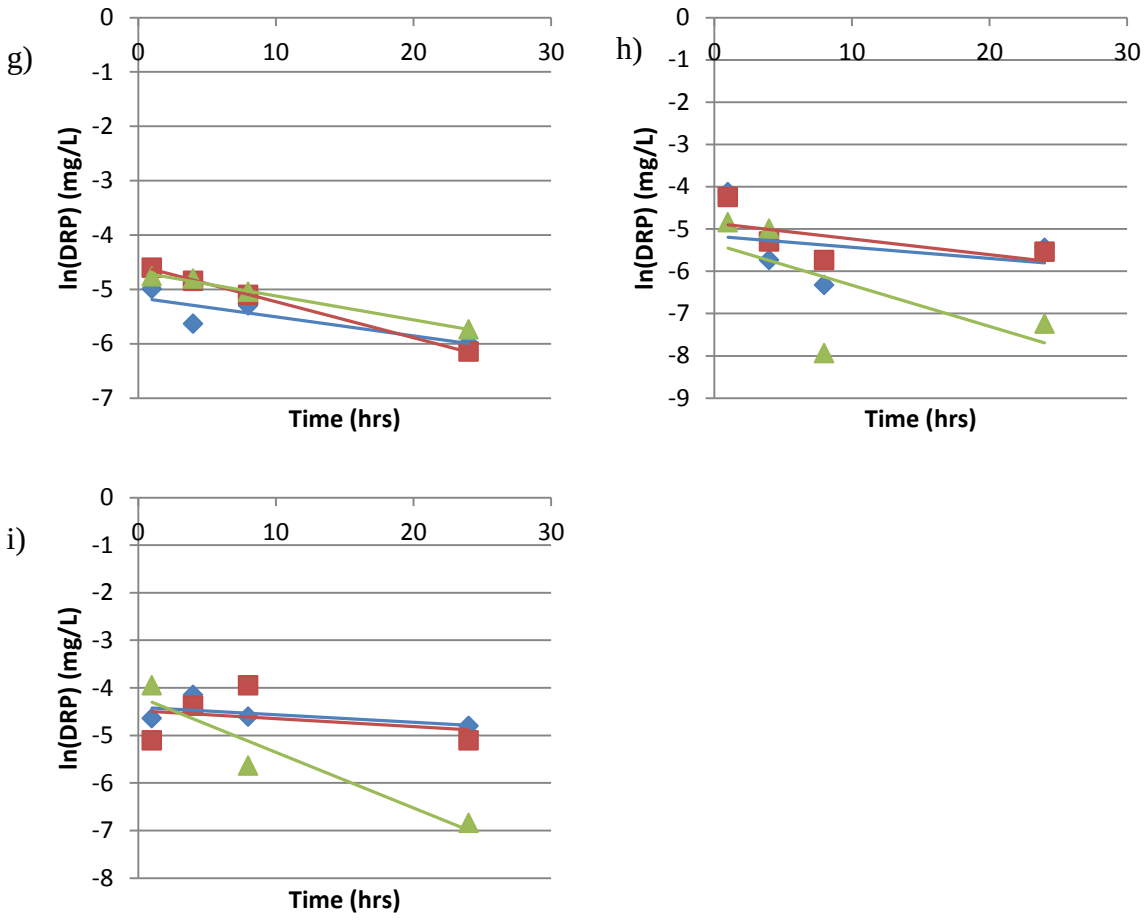


Fig. A1 Uptake kinetics in the microcosm uptake experiments

a) Salt pond, 50 µg/L spiked microcosms. Data for 3 replicates and the control sample with no microbial mat. Linear regression R^2 values = 0.99, 0.73, 0.96 and 0.90 for the A, B, C microcosms and the control microcosm respectively.

b) Skua pond, 5 µg/L spiked microcosms. Data for 3 replicates with microbial mat present. Linear regression R^2 values = 0.50, 0.75, 0.82 and 0.15 for the A, B, C microcosms and the control microcosm respectively.

c) Orange pond, 50 µg/L spiked microcosms. Data for 3 replicates and the control sample with no microbial mat. Linear regression R^2 values = 0.75, 0.90, and 0.92 for the A, B, C microcosms respectively.

d) Morepork pond, 50 µg/L spiked microcosms. Data for 3 replicates and the control sample with no microbial mat. Linear regression R^2 values were all below 0.24.

e) Finch pond, 50 µg/L spiked microcosms. Data for 3 replicates and the control microcosm with no microbial mat. Linear regression R^2 values = 0.72, 0.35, 0.78 and 0.09 for the A, B, C microcosms and the control microcosm respectively.

f) Canary pond, 50 µg/L spiked microcosms. Data for 3 replicates and the control sample with no microbial mat. Linear regression R^2 values were all below 0.4.

g) E4 pond, 50 µg/L spiked microcosms. Data for 3 replicates. Linear regression R^2 values = 0.69, 0.99, and 0.99 for the A, B, C microcosms respectively.

h) L16 pond, 50 µg/L spiked microcosms. Data for 3 replicates. Linear regression R^2 values were all below 0.4.

i) L26 pond, 50 µg/L spiked microcosms. Data for 3 replicates. Linear regression R^2 values = 0.90 in the C microcosm, the A and B microcosms R2 < 0.4.

Appendix 3 – Short term monitoring DRP vs parameters

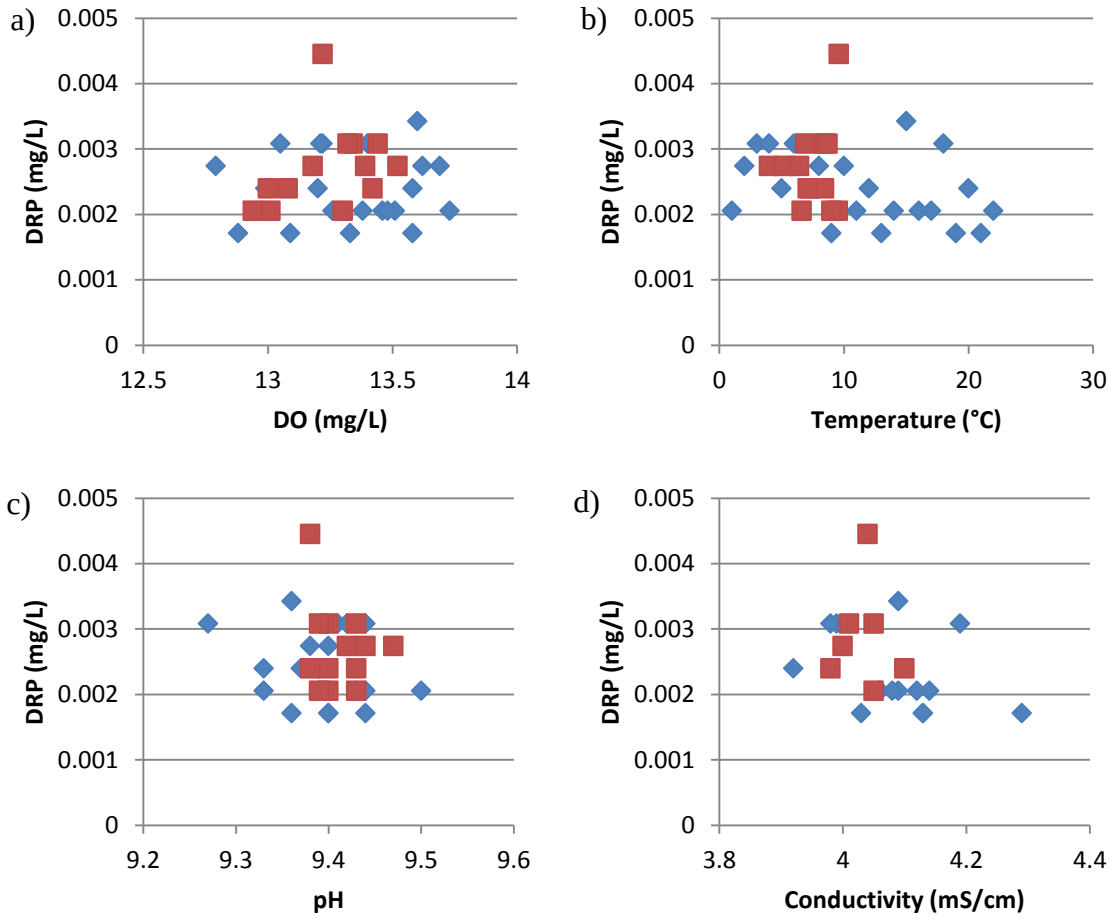


Fig A2. The physico-chemical parameters in Morepork pond over 24 hours versus pond DRP concentration. Blue diamonds represent samples from the pond surface, and red squares are taken from the base of the pond.

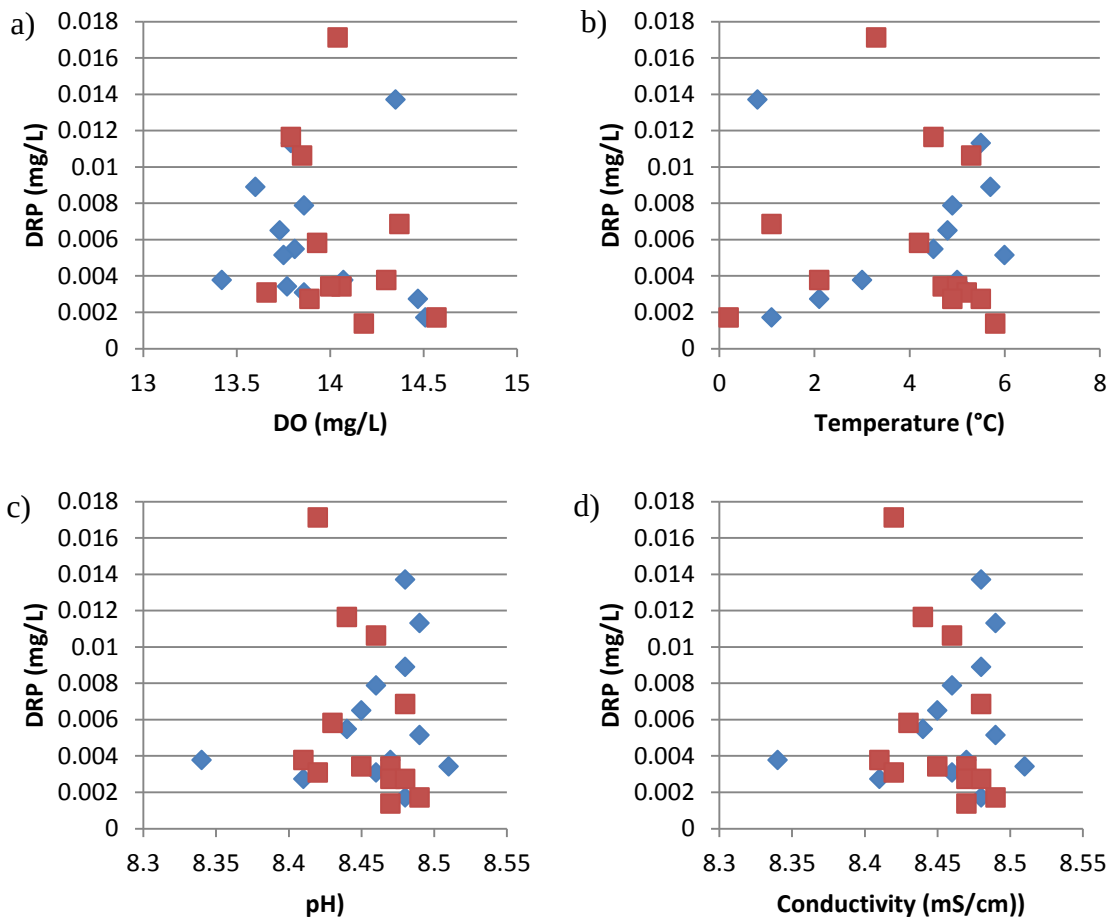


Fig A3. The physico-chemical parameters in Camp Pond over 12 hours versus pond DRP concentration. Blue diamonds represent samples from the pond surface, and red squares are taken from the base of the pond.

Appendix 4 – Water column P vs conductivity and ions

Graphs which compare data from every pond studied at each sample site, plotting water column P concentrations against conductivity and calcium concentrations.

Graphs of log transformed concentration of DRP over time in the microcosms that were spiked with 5 or 50 µg/L DRP in the uptake experiments.

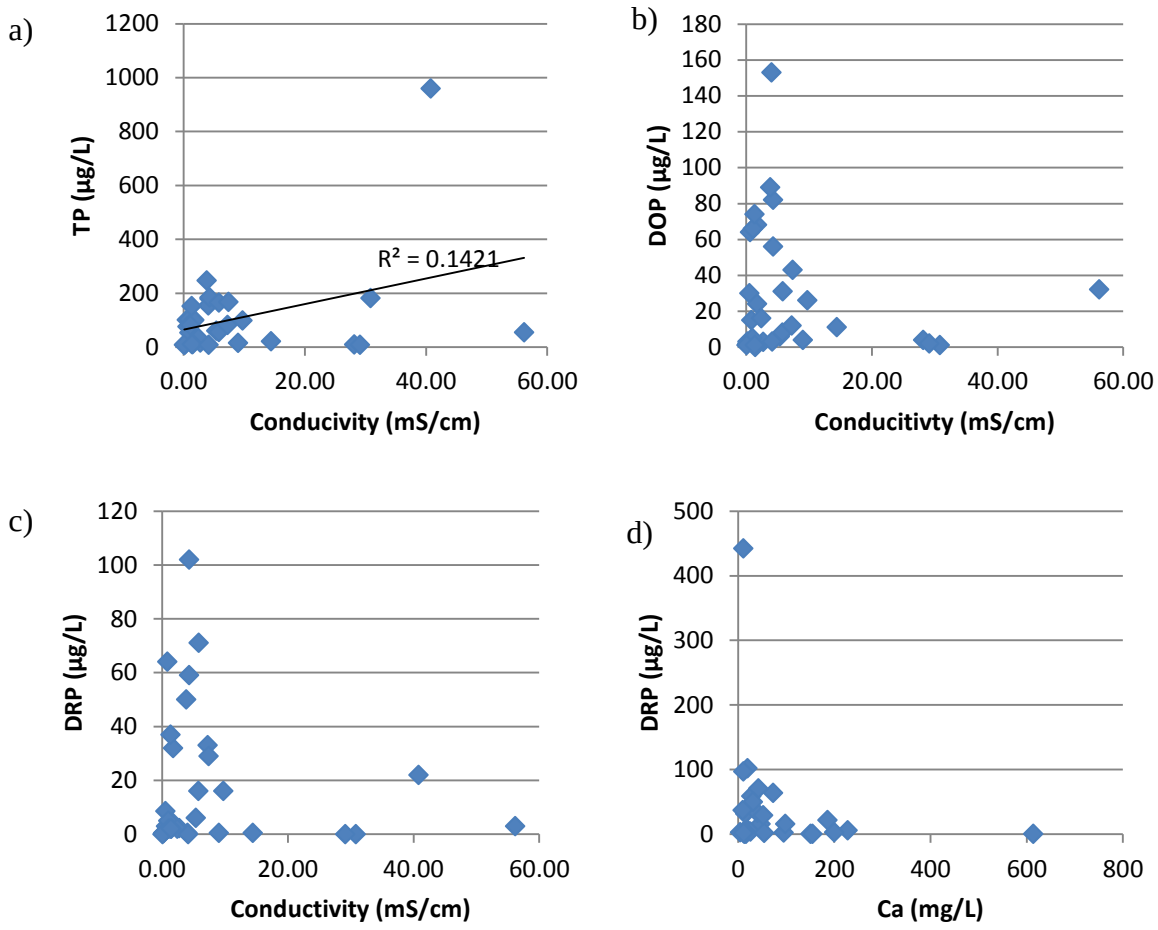


Fig A4. Water column chemistry parameters versus water column P concentrations at all study sites.
a) Total P vs conductivity all ponds
b) DOP vs conductivity all ponds
c) DRP vs conductivity all ponds
d) Ca vs DRP all ponds

Appendix 5 – Major ion data

Table A2. Major ion data for ponds, soils and pore waters. Soil major ions were measured on a 1:5 soil:deionized water leach that was shaken for 1 hour. Soils are noted by 'soil', and porewaters have 'PW' and the depth they were sampled from. Samples with 'SP' are soils from Bratina Island where 'SP' denotes skua guano was present on the soil, while 'SPC' is a non-guano affected control. Blank cells had concentrations below detection, and 'na' means not analysed.

Sampled	Site	Pond	Fluoride	Chloride	Bromide	Nitrate	Sulfate	Phosphate	HCO3	Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Jan-11	Bratina Island	Brack	0.33	1135.83	2.22		6328.24	0.219			3600.00		63.00	109.00	97.00
Jan-11	Bratina Island	Casten	0.39	178.43	0.17	1.41	214.51	0.454			250.00		7.30	9.30	9.10
Jan-11	Bratina Island	Conophyton	0.22	99.55			47.47				92.00		4.80	7.90	8.70
Jan-11	Bratina Island	Duet	0.14	19.77		0.54	21.11	0.029			23.00		1.01	2.10	2.40
Jan-11	Bratina Island	Fogghorne	0.16	104.58			27.78				113.00		4.90	5.00	5.80
Jan-11	Bratina Island	Fogghorne Soil	0.28	18.65		1.09	24.30	3.051			40.00		5.60	5.50	2.10
Jan-11	Bratina Island	Fresh	0.27	87.99			95.85	0.020			101.00		3.10	5.90	7.00
Jan-11	Bratina Island	Fresh Soil	0.30	331.24	0.36	12.56	197.92	0.478			270.00		13.30	17.30	27.00
Jan-11	Bratina Island	Nostoc	0.28	176.12		0.51	21.02	0.084			129.00		5.40	10.50	8.20
Jan-11	Bratina Island	Orange	0.34	491.50	0.65		83.93				370.00		14.30	18.70	10.20
Jan-11	Bratina Island	Orange Soil	0.39	15.55		2.52	23.61	3.736			48.00		6.80	6.60	2.50
Jan-11	Bratina Island	P70	0.42	2033.13	0.29	0.04	286.22				1300.00		50.00	118.00	58.00
Jan-11	Bratina Island	P70e	0.30	4297.60	12.22	0.33	401.19				1930.00		72.00	400.00	330.00
Jan-11	Bratina Island	Salt	2.11	8820.33	26.79		25268.18	0.000			15900.00		420.00	460.00	230.00
Jan-11	Bratina Island	Skua	0.25	134.28		0.67	217.47	0.295			181.00		6.10	8.20	12.10
Jan-11	Cape Evans	Pond 1	0.90	953.21	1.08	0.15	60.30				550.00		50.00	77.00	34.00
Jan-11	Cape Evans	Pond 2	0.82	2233.47	4.13		117.04	0.171			1350.00		89.00	170.00	42.00
Jan-11	Cape Evans	Pond 2 Soil	1.40	125.95	0.14	6.08	219.94	0.206			134.00		10.80	9.50	61.00
Jan-11	Cape Evans	Pond 3	0.81	3169.48	0.32		399.52	0.214			1830.00		103.00	250.00	98.00
Jan-11	Cape Evans	Pond 9	0.23	1018.78	1.82		223.59	0.103			1090.00		43.00	130.00	52.00
Jan-11	Cape Evans	Snow 1		32.40		0.05	4.22				8.90		0.43	1.13	0.72
Jan-11	Cape Evans	Snow 2		96.92		0.13	3.24				6.80		0.40	0.96	0.57
Jan-11	Cape Royds	Bart	3.75	20994.62			1889.33				11500.00		1880.00	1320.00	200.00
Jan-11	Cape Royds	Bart Soil	2.86	480.48		0.24	1404.92				950.00		35.00	18.00	55.00
Jan-11	Cape Royds	Ernest	1.96	647.13	0.13	0.42	88.42				310.00		69.00	40.00	54.00
Jan-11	Cape Royds	Green	1.21	1101.45	1.79		143.55	0.615			750.00		101.00	69.00	20.00
Jan-11	Cape Royds	Nimrod	1.34	2424.12	3.40	0.05	345.50	0.124			1320.00		105.00	152.00	40.00
Jan-11	Cape Royds	Nimrod Soil	0.87	757.50	0.60	0.18	176.18	0.691			710.00		66.00	15.00	8.00
Jan-11	Cape Royds	Shackleton	0.95	282.46	0.13		32.07				153.00		31.00	16.80	11.90
Jan-11	Cape Royds	Shackleton Soil	0.47	398.04		8.74	37.40	0.833			200.00		85.00	14.70	3.50
Jan-11	Cape Royds	Snow 0-10 cm depth	0.05	0.74		0.21	0.46				0.41		0.07	0.09	0.08
Jan-11	Cape Royds	Snow 10-20 cm depth		11.50			1.71				7.30		0.50	0.88	0.97
Jan-11	Cape Royds	Coast									159.00		16.00	18.60	7.40

Sampled	Site	Pond	Fluoride mg/L	Chloride mg/L	Bromide mg/L	Nitrate mg/L	Sulfate mg/L	Phosphate mg/L	HCO3 mg/L	Lithium mg/L	Sodium mg/L	Ammonium mg/L	Potassium mg/L	Magnesium mg/L	Calcium mg/L
Jan-12	HPP	HP1	0.97	1005.01	1.59	0.58	423.51		231.86		656.32		41.43	95.62	56.40
Jan-12	HPP	HP2	0.70	505.07	1.17	0.20	410.01		287.51		485.63	0.725	15.11	34.60	17.60
Jan-12	HPP	HP2 soil	0.32	27.68	0.04	1.61	19.20		0.00		35.30		4.25	1.91	3.76
Jan-12	HPP	HP3	0.25	160.04	0.44	0.38	74.14		100.47		119.73	0.094	6.14	13.94	19.40
Jan-12	HPP	Ob Hill snow	0.00	0.60	0.00	0.23	0.50		0.00		0.40		0.03	0.04	0.05
Jan-12	HPP	OHP	0.44	174.28	0.42	0.20	31.57		183.94		116.35		10.79	14.53	14.72
Jan-12	HPP	OHP soil	1.37	108.69	0.22	58.19	91.40		0.00		116.90	0.034	16.82	1.96	1.86
Jan-12	LW	Lake Brownworth	0.06	3.63	0.00	0.04	2.19		14.61		2.57	0.186	0.57	0.64	2.37
Jan-12	LW	LW12	6.41	6385.47	0.00	311.23	1946.38		90.43		3019.94	0.083	412.40	753.66	614.35
Jan-12	LW	LW12 soil	0.45	188.77	0.06	19.88	104.36		0.00		94.82	0.004	15.64	19.25	47.60
Jan-12	LW	LW13	1.89	4325.51	1.07	303.74	228.62		62.60		1788.96	0.178	177.37	543.70	150.56
Jan-12	LW	Lw13 soil	0.74	27.78	0.00	5.00	53.76		0.00		33.98		12.22	3.30	11.79
Jan-12	LW	LW14	2.99	2201.04	0.49	12.36	804.55		110.13		1063.12		126.46	230.53	228.38
Jan-12	LW	LW14 soil	3.23	848.96	0.08	25.10	1142.43		0.00		523.89		85.25	46.05	427.89
Jan-12	LW	LW15	1.95	1065.33	0.24	7.06	314.57		78.83		517.66	7.013	62.84	109.96	94.60
Jan-12	LW	LW15 soil	0.22	5.90	0.00	0.78	6.85		0.00		9.00		4.06	1.07	5.07
Jan-12	LW	LW16 neat	0.50	84.43	0.00	2.81	28.51		9.27		47.02	0.141	4.65	12.01	16.26
Jan-12	LW	LW16 soil	0.39	40.18	0.00	4.56	23.13		0.00		27.41	0.018	5.43	3.21	10.25
Jan-12	LW	LW18 neat	0.29	64.34	0.00	0.05	35.36		2.90		46.77	0.149	3.09	5.54	12.72
Jan-12	LW	LW18 soil	0.40	6.40	0.00	0.22	15.49		0.00		19.29		3.11	0.46	5.46
Jan-12	LW	LW2	11.50	14533.05	4.76	67.38	2385.67		164.62		6742.45		805.52	1629.94	664.39
Jan-12	LW	LW2 soil	0.97	66.73	0.00	5.09	196.68		0.00		75.15		17.95	5.29	57.44
Jan-12	LW	LW7	1.07	215.94	0.07	7.69	140.66		250.41		120.88		15.53	32.72	72.82
Jan-12	LW	LWG ice	0.01	1.24	0.00	0.10	0.47		0.00		0.89	0.122	0.20	0.07	0.06
Jan-12	UW	UW Snow	0.03	2.19	0.00	1.53	1.21		0.00		1.09		0.03	0.59	0.27
Jan-12	UW	UWG Ice	0.02	0.49	0.00	0.13	0.31		0.00		0.21	0.010	0.08	0.02	0.04
Jan-12	UW	E4 soil	2.48	47.06	0.00	38.15	218.14		0.00		48.37	0.106	2.33	15.54	66.09
Jan-12	UW	E9 soil	0.42	7.57	0.00	7.55	14.76		0.00		7.17	0.029	0.87	2.81	2.87
Jan-12	UW	L4 soil	0.56	26.28	0.00	20.52	52.31		0.00		21.59	0.012	0.83	10.03	11.79
Jan-12	UW	L9 soil	0.35	12.59	0.00	7.62	2.89		0.00		14.75		0.28	0.76	0.22
Jan-12	UW	L15 soil	0.49	6.98	0.00	4.52	17.68		0.00		18.04		0.50	1.60	1.33
Jan-12	UW	L16 soil	0.64	4.12	0.00	2.42	11.51		0.00		9.85	0.018	0.81	2.30	2.57
Jan-12	UW	L26 soil	0.59	40.30	0.00	23.72	29.14		0.00		38.22		0.95	4.97	2.40
Jan-12	UW	E4	3.35	225.86	0.06	195.48	937.42		27.82		290.22	0.050	2.75	71.95	234.15
Jan-12	UW	E4 ppt	2.49	152.32	0.00	137.44	591.38		0.00		211.67	0.044	2.07	48.86	147.81
Jan-12	UW	L15	5.58	530.78	0.31	396.63	1360.11		310.69		548.09	0.043	5.51	236.16	242.49
Jan-12	UW	L16	2.25	1316.34	0.43	887.80	287.96		140.28		692.61	0.547	10.92	354.80	61.25
Jan-12	UW	L9	7.25	12558.26	0.00	7460.19	1735.43		426.62		6197.81	0.199	37.19	3516.04	312.85
Jan-12	UW	L26	8.43	11609.88	0.00	6692.33	2594.12		688.63		5886.90	0.185	35.28	3266.95	305.36

Sampled	Site	Pond	Fluoride mg/L	Chloride mg/L	Bromide mg/L	Nitrate mg/L	Sulfate mg/L	Phosphate mg/L	HCO3 mg/L	Lithium mg/L	Sodium mg/L	Ammonium mg/L	Potassium mg/L	Magnesium mg/L	Calcium mg/L
Jan-13	MIS	BI bulk soil		1914.35	1.52	106.57	1190.60				908.35		35.84	196.46	505.29
Jan-13	MIS	Camp		2370.80	4.41		523.77			0.006	1232.94	n.a.	57.20	258.00	91.31
Jan-13	MIS	Fogghorne		245.55	0.62	0.13	76.67	0.014		0.004	242.00		9.73	7.64	9.87
Jan-13	MIS	Huey		1459.06	4.25		164.20			0.016	844.34	n.a.	30.16	125.58	13.07
Jan-13	MIS	Huey brine		27469.00	61.05		4617.56				17070.25		438.84	2322.19	73.69
Jan-13	MIS	Orange		452.15	1.15	n.a.	91.69	0.037		0.006	372.83	n.a.	15.66	16.25	8.60
Jan-13	MIS	P70		1007.26	2.86	0.02	225.43	0.058		0.008	667.00	n.a.	29.35	65.00	31.30
Jan-13	MIS	Russell		107.51	0.25	0.37	286.54	0.146		0.002	198.54	n.a.	5.27	7.12	9.45
Jan-13	MIS	Salt		4209.86	6.90		21294.18			0.088	12594.49	n.a.	260.86	273.74	185.90
Jan-13	MIS	Skua		106.61	0.25	1.05	192.72	0.292		0.002	159.00		5.47	7.83	10.80
Jan-13	MV	BE under mat		6947.03	9.70	n.a.	4595.59	1.302		0.030	3035.89		123.70	101.31	26.65
Jan-13	MV	Bidseye base		15733.41	23.89		10647.82			0.080	6666.44		272.95	193.01	21.11
Jan-13	MV	Birsdeye surface		2722.42	6.75		2734.75	0.526		0.119	15131.09		583.04	463.30	18.47
Jan-13	MV	Canary		779.58	1.08	0.95	611.03	0.503		0.004	868.75		28.78	n.a.	n.a.
Jan-13	MV	Canary brine		1194.17	1.12		783.83			0.078	13720.69		325.72	647.24	308.74
Jan-13	MV	Finch		414.80	0.68	0.03	122.79	0.023		0.004	313.71		20.96	20.93	23.86
Jan-13	MV	Kingfisher		147.98	0.24	1.35	139.88	0.095		0.002	176.39		9.73	11.21	13.46
Jan-13	MV	Macaw		1541.51	4.37	0.03	386.19	0.151			1108.10		56.28	47.73	47.08
Jan-13	MV	Macaw brine		10205.98	21.53	0.87	2557.56			0.080	7191.95		266.46	341.40	265.01
Jan-13	MV	Miers snow		2.48		0.16	1.02				1.90		0.10	0.13	0.20
Jan-13	MV	Miers Stream		33.62	0.07		29.22			0.001	26.57		2.70	2.92	23.73
Jan-13	MV	Morepork		1036.83	1.81	0.03	262.68			0.013	1082.64		66.03	153.50	155.00
Jan-13	MV	Morepork brine		38099.69	44.94		12097.30			0.289	22743.39		1029.55	3461.45	815.46
Jan-13	MV	Robin		126.93	0.17		39.08				122.54	0.046	6.19	3.03	4.33
Jan-13	MV	Robin brine		1755.83	2.31		347.73			0.002	1286.56		52.79	41.29	12.50
Jan-13	MIS	FH PW 10-11		299.02	0.49	0.70	46.29				19.38		1.77	2.17	3.44
Jan-13	MIS	FH PW 11-12		318.88	0.53	0.57	41.42				28.45		2.26	3.55	2.16
Jan-13	MIS	FH PW 12-13		308.31	0.71	1.01	59.65	0.862			47.20	0.163	3.88	7.05	4.48
Jan-13	MIS	OR PW 1-2		442.76	0.93	1.19	1.23	0.159			126.48		6.95	28.31	7.10
Jan-13	MIS	OR PW 2-3		431.68	0.94		89.70				55.86		3.02	4.24	1.92
Jan-13	MIS	OR PW 3-4		447.01	0.94		71.15				22.04		1.22	0.63	0.63
Jan-13	MIS	OR PW 4-5		431.66	0.76		81.75				38.28		1.70	0.55	0.56
Jan-13	MIS	OR PW 5-6		391.72	0.73		149.75				42.70		2.10	1.26	0.94
Jan-13	MIS	OR PW 6-7		365.70	0.61	0.46	171.40	0.152			23.47		1.38	0.91	0.73
Jan-13	MIS	OR PW 7-8		361.00	0.72	0.87	95.48	0.000			32.33		1.61	0.84	0.68
Jan-13	MIS	OR PW 8-9		370.49	0.47	0.77	77.76				22.87		1.33	0.76	0.63
Jan-13	MIS	OR PW 9-10		425.73	0.90	1.77	99.53				14.98		0.66	0.37	0.25

Sampled	Site	Pond	Fluoride mg/L	Chloride mg/L	Bromide mg/L	Nitrate mg/L	Sulfate mg/L	Phosphate mg/L	HCO3 mg/L	Lithium mg/L	Sodium mg/L	Ammonium mg/L	Potassium mg/L	Magnesium mg/L	Calcium mg/L
Jan-13	MIS	P70 PW 0-1		879.41	1.86	7.01	178.74				61.90		3.40	4.71	2.18
Jan-13	MIS	P70 PW 1-2		873.43	1.59	32.74	440.13				23.29		1.51	1.61	1.54
Jan-13	MIS	P70 PW 2-3		720.04	1.62	0.42	180.91	0.086			100.74		4.42	2.90	1.44
Jan-13	MIS	P70 PW 3-4		725.03	1.49	1.03	308.26	0.093			45.03		2.20	1.86	1.06
Jan-13	MIS	P70 PW mat		922.57	2.42	0.42	4.52	1.243			369.29		77.87	174.17	26.87
Jan-13	MIS	SP1		62.24	0.23	0.03	97.45		na	na	na	na	na	na	na
Jan-13	MIS	SP1C		94.41	0.26	15.86	86.28	2.054	na	na	na	na	na	na	na
Jan-13	MIS	SP2		44.83	0.09		53.58	42.819	na	na	na	na	na	na	na
Jan-13	MIS	SP2C		16.15	0.03	2.01	22.50	2.688	na	na	na	na	na	na	na
Jan-13	MIS	SP3		140.53	0.44	0.07	86.40	49.091	na	na	na	na	na	na	na
Jan-13	MIS	SP3C		63.86	0.16	6.05	33.21	2.938	na	na	na	na	na	na	na
Jan-13	MIS	SP4		27.05		0.01	42.19		na	na	na	na	na	na	na
Jan-13	MIS	SP4C		105.91	0.23	5.04	38.25	1.453	na	na	na	na	na	na	na
Jan-13	MIS	FH soil 1m		121.06	0.30	24.16	37.97	0.775	na	na	na	na	na	na	na
Jan-13	MIS	FH soil 2m		239.32	0.72	13.13	238.60	0.899	na	na	na	na	na	na	na
Jan-13	MIS	FH soil 3m		32.88	0.10	4.36	34.98	3.143	na	na	na	na	na	na	na
Jan-13	MIS	FH soil 5m		218.82	0.58	6.31	122.40	0.771	na	na	na	na	na	na	na
Jan-13	MIS	P70 soil 1m		422.84	1.10	66.59	790.64	0.948	na	na	na	na	na	na	na
Jan-13	MIS	P70 soil 2m		128.98	0.36	28.68	74.92	0.795	na	na	na	na	na	na	na
Jan-13	MIS	P70 soil 5m		315.36	0.87	24.80	250.01	0.404	na	na	na	na	na	na	na
Jan-13	MIS	P70 soil 8m		319.99	0.72	14.83	202.43	0.312	na	na	na	na	na	na	na
Jan-13	MV	Clau		1744.65	3.24		1375.16	0.145	na	na	na	na	na	na	na
Jan-13	MV	Clau brine		16449.55	22.97		12634.46		na	na	na	na	na	na	na
Jan-13	MV	Fantail		576.53	0.90	0.55	168.72	0.840	na	na	na	na	na	na	na
Jan-13	MV	Fantail brine		2720.35	3.68	3.73	745.93	0.579	na	na	na	na	na	na	na
Jan-13	MV	Kiwi		619.70	1.31	0.01	241.80	0.169	na	na	na	na	na	na	na
Jan-13	MV	Kiwi brine		769.52	1.70	1.25	280.82	0.557	na	na	na	na	na	na	na
Jan-13	MV	Moa		285.72	0.58		116.27	0.038	na	na	na	na	na	na	na
Jan-13	MV	Sparrow		369.11	0.58	0.02	147.36	0.176	na	na	na	na	na	na	na
Jan-13	MV	Sparrow brine		5426.92	5.96	1.09	2857.34	0.905	na	na	na	na	na	na	na
Jan-13	MV								na	na	na	na	na	na	na
Jan-13	MV	CAN soil 1m		1052.57	0.75	48.09	1282.03	0.954	na	na	na	na	na	na	na
Jan-13	MV	CAN soil 2m		143.62		5.91	339.84	3.018	na	na	na	na	na	na	na
Jan-13	MV	CAN soil 5m		287.06	0.13	4.60	197.70	0.772	na	na	na	na	na	na	na
Jan-13	MV	CAN soil 8m		65.09		3.21	126.46	1.595	na	na	na	na	na	na	na
Jan-13	MV	MAC soil 1m		316.68	0.34	19.41	243.99	1.519	na	na	na	na	na	na	na
Jan-13	MV	MAC soil 3m		773.90	0.60	41.18	838.73	2.697	na	na	na	na	na	na	na
Jan-13	MV	MAC soil 7m		38.44		1.37	34.46	2.528	na	na	na	na	na	na	na
Jan-13	MV	MAC soil 13m		1115.24	0.42	29.63	89.82	0.127	na	na	na	na	na	na	na

Appendix 6 – Soil salt analyses

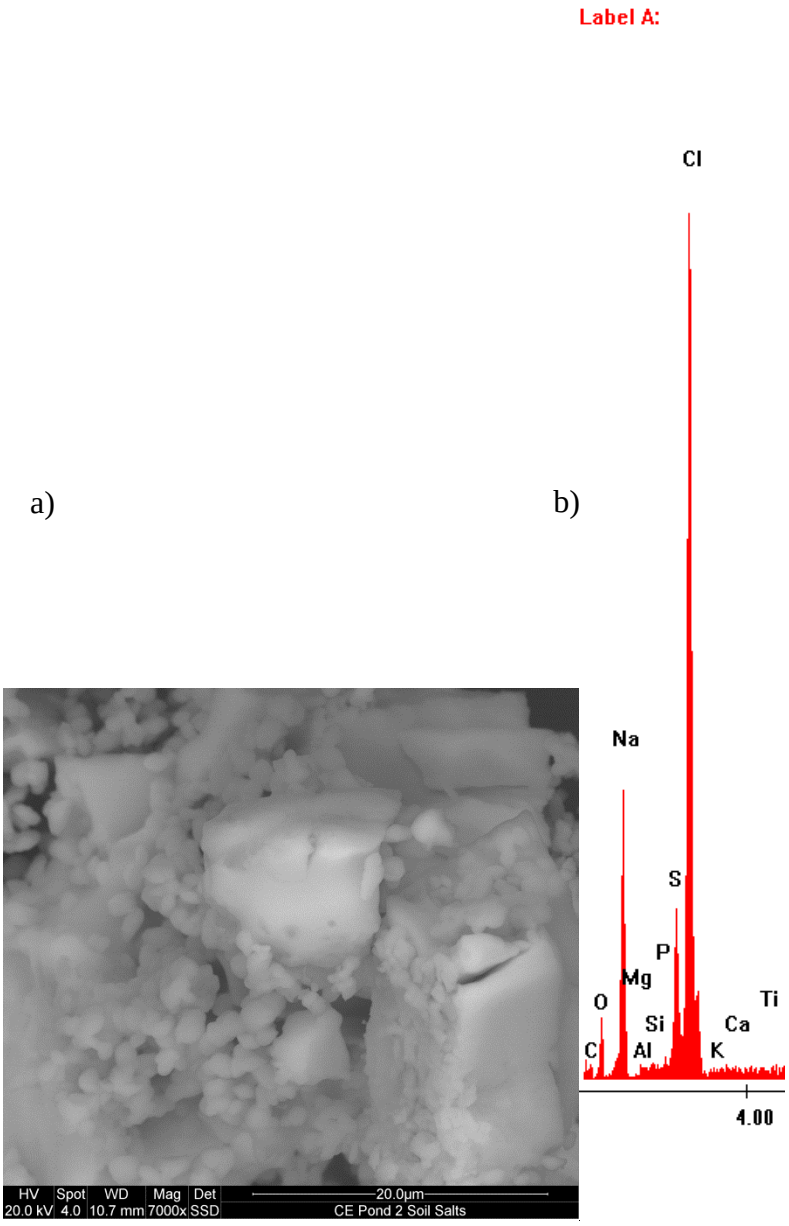


Fig A5. Halite crystals collected from Pond 2 at Cape Evans a) halite crystals b) EDS spectrum of the crystal

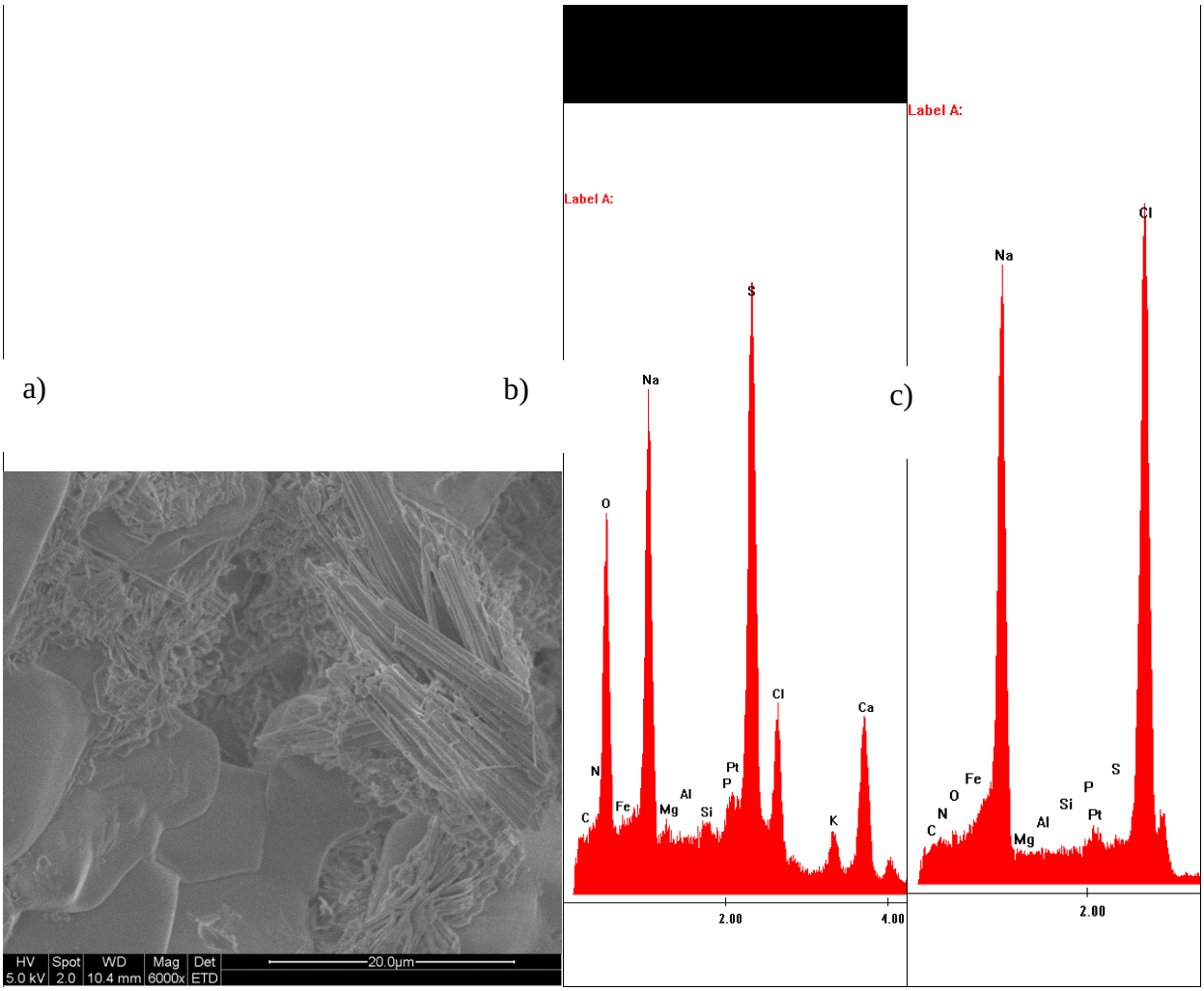


Fig A6. Halite and mirabilite collected from Bart Pond at Cape Royds. A) Long thin mirabilite crystals, with block like halite, b) EDS spectrum of mirabilite and c) EDS spectrum of Halite

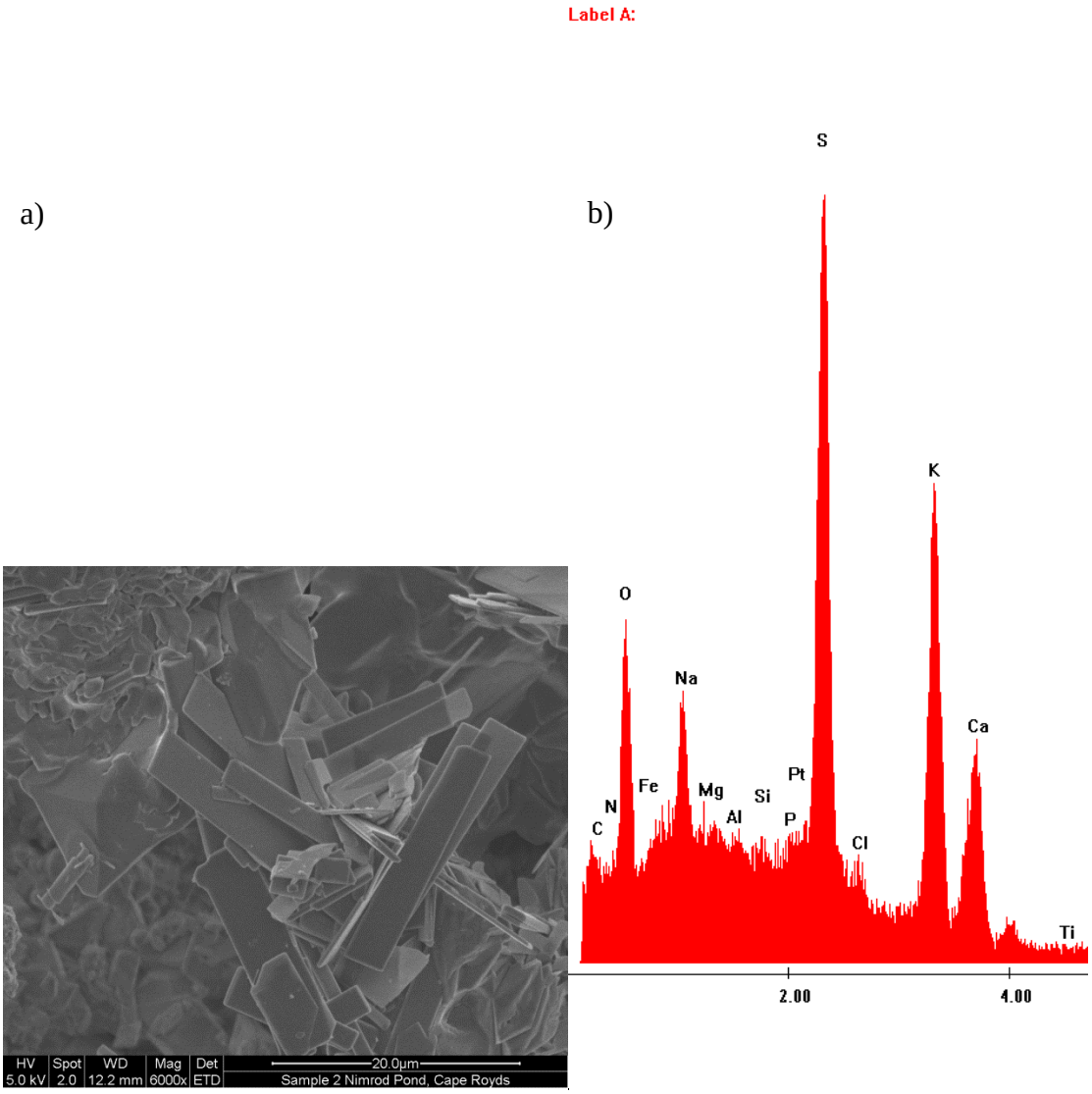


Fig A7. a) Unidentified salt crystals collected from Ernest Pond at Cape Royds, and b) the EDS spectrum, indicating K, Ca, Na and SO_4 composition.

Appendix 7 – Miers Valley Stratification

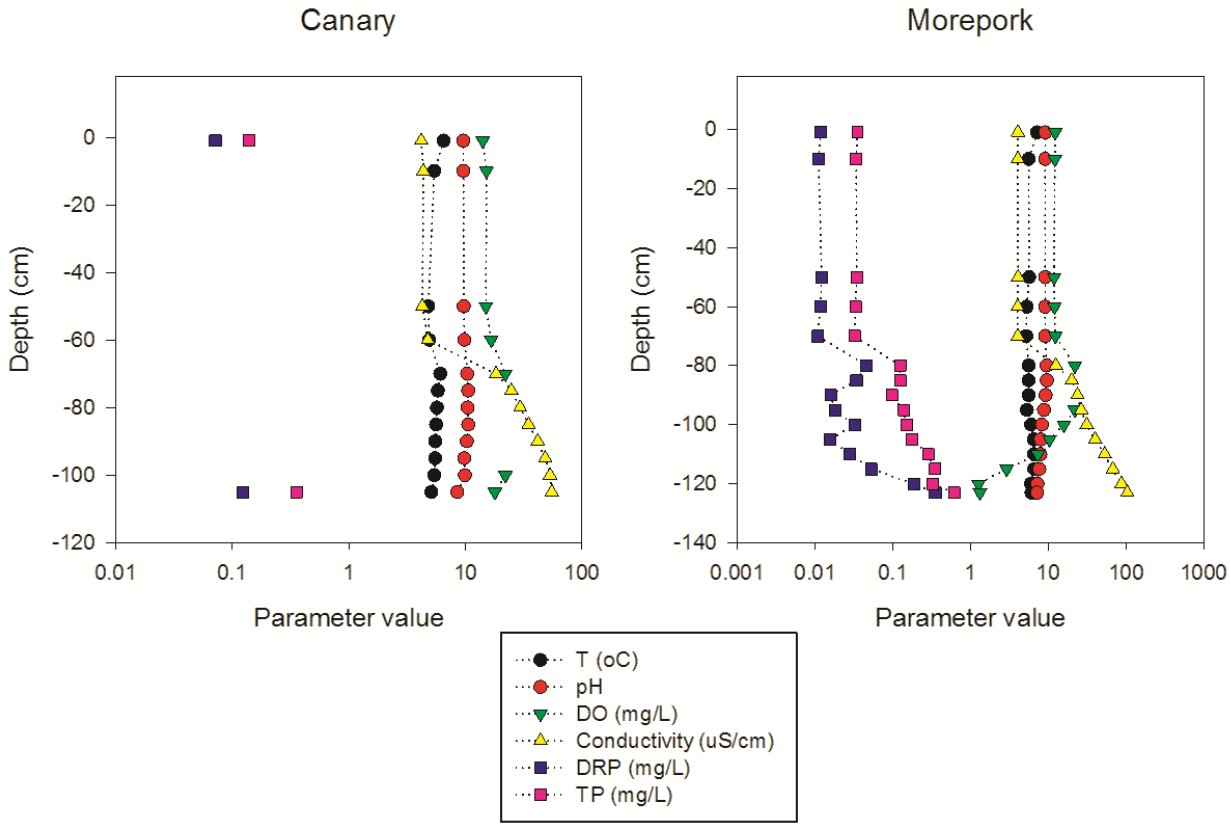


Fig. A8. Depth profiles of key parameters in two stratified ponds. The unit for each parameter is displayed on the legend. The DO meter had a maximum reading of 22 mg/L, which was exceeded from 70 to 100 cm depth in Canary pond, and from 80 to 95 cm depth in Morepork pond.

b) Canary pond b) Morepork pond